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THE ORGANOMETALLIC CHEMISTRY OF
CONJUGATED, LOW-COORDINATE
PHOSPHACARBON COMPOUNDS

BY
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SUBMITTED FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

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I hereby declare that the work reported herein is my own unless otherwise stated and has not been previously submitted, in this form or any other, for a degree at any institution. All of the work reported was carried out under the supervision of Dr I. R. Crossley between October 2010 and September 2014.

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SUMMARY

Organometallic complexes incorporating low-coordinate phosphorus have been synthesised with a view to better understanding the physical and electronic properties and reactivity of such compounds, along with synthetic methodologies to furnish them.

Novel ruthenium complexes of the type $[\text{Ru}(\text{CO})\{\kappa^3\text{-}N,C,P\text{-P}(\text{Pz}^{\text{R}''})\text{CH}(\text{R})\}(\text{PPh}_3)_2]$ (Pz = pyrazolyl) have been synthesised *via* addition of pyrazolates to complexes of the type $\text{RuCl}(\text{CO})(\text{PPh}_3)_2(\text{P}=\text{CHR})$. The general structure of the resultant products was elucidated, with a Ru–C–P three-membered ring and bridging pyrazolyl unit confirmed by heteronuclear NMR spectroscopy and X-ray diffraction studies. The nature of the R groups was found to affect the nature of the P–C bond, which lies between a typical single and double P–C bond. The formation of these complexes demonstrated for the first time the ambiphilic nature of the parent ruthenaphosphaalkenyl systems, which was explored by both DFT calculations and their reactivity upon addition of various nucleophiles and electrophiles.

A range of extended π -systems have been sought for their potential utility in the synthesis of phosphapolyynyl fragments. Complexes of the type $[\text{Tp}'\text{M}(\text{CO})_2(\equiv\text{CC}\equiv\text{CR})]$ were pursued, (where $\text{R} = \text{CO}_2\text{R}'$) *via* a variety of synthetic protocols including traditional Sonogashira methodologies, *in situ* formation of the propargylidyne moiety ($\text{M}\equiv\text{C}\equiv\text{C}-$) and cross-coupling reactions between a terminal alkyne and $\text{Au}(\text{PPh}_3)$ -terminated propargylidynes. Additionally, a range of metal–alkynyl complexes were pursued *via* vinylidene/alkyne tautomerism reactions. In particular, the successful synthesis of a range of complexes of the type $[\text{RuCl}(\text{dppe})_2(=\text{CH}=\text{CR})][\text{OTf}]$ and $[\text{RuCl}(\text{dppe})_2(\text{C}\equiv\text{CR})]$ is discussed with characterization of the novel compounds by IR and heteronuclear NMR spectroscopies, mass spectrometry and X-ray diffraction studies.

Finally, synthesis of a novel series of cyaphide-containing compounds is demonstrated. The physical and chemical properties of this elusive ligand are discussed and the electronic properties studied computationally. Attempts were also made to furnish complexes with η^1 -coordination of the phosphorus lone pair to a second metal centre, *i.e.* complexes of the type $[(\text{dppe})_2(\text{RC}\equiv\text{C})\text{Ru}-\text{C}\equiv\text{P}-\text{ML}_n]$.

ABBREVIATIONS

d	Doublet
DBN	1,5-Diazabicyclo[4.3.0]non-5-ene
DCM	Dichloromethane
DMF	Dimethyl formamide
DABCO	1,4-diazabicyclo[2.2.2]octane
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
dmp	2,6-dimesitylphenyl
dppe	1,2-bis(Diphenylphosphino)ethane
dppm	Diphenylphosphinomethane
Et	Ethyl
IPA	Propan-2-ol
m	Multiplet
Me	Methyl
Mes	2,4,6-trimethyl phenyl
Mes*	2,4,6-tri-tert-butyl phenyl
mt	Methimazole
N ₃ N	(Me ₃ SiNCH ₂ CH ₂) ₃ N
OTf	Trifluoromethanesulfonate
Ph	Phenyl
Pz	Pyrazolyl
Pz ^{(CF₃)₂}	3,5-bis(trifluoromethyl)pyrazolyl
Pz ^(CF₃)	3-(trifluoromethyl)pyrazolyl
Pz ^(tBu)	3-tert-butyl-1H-pyrazolyl
Pz ^(Me, CF₃)	3-methyl-5-(trifluoromethyl)pyrazolyl
Pz ^(tBu₂)	3,5-di-tert-butyl-1H-pyrazolyl
Pz*	3,5-dimethylpyrazolyl
q	Quartet
qnt	Quintet
s	Singlet
t	Triplet
TBAF	Tetrabutylammonium fluoride
TBAT	Tetrabutylammonium triphenylsilyldifluorosilicate
^t Bu	Tertiary butyl
TFAA	Trifluoroacetic anhydride
THF	Tetrahydrofuran
tht	Tetrahydrothiophene
TMS	Trimethylsilyl
Tp	[HB(pz) ₃] [−]
Tp*	[HB(pz*) ₃] [−]
triphos	(CH ₂ Ph ₂ P) ₃ –CMe
Xyl	2,6-dimethylphenyl

LIST OF FIGURES

Figure 1: An $\eta^1:\eta^6$ -coordinated phosphabenzene ($M = M' = \text{Cr}$; $M = M' = \text{Mo}$; $M = \text{Cr}$, $M' = \text{W}$)	4
Figure 2: Products from the reaction of $[(\text{C}_5\text{H}_5)(\text{CO})_5\text{Fe}(\text{P}(\text{SiMe}_3)-\text{P}=\text{C}(\text{SiMe}_3)_2)]$ and $[\text{Cr}(\text{C}_8\text{H}_{14})(\text{CO})_5]$. ⁴⁶	7
Figure 4: The first diphosphaallene coordination compound ⁸¹	11
Figure 5: The Five Bonding Modes of Coordinated Phosphaalkenes	16
Figure 6: $\text{FeBr}(\text{BPEP})$	19
Figure 7: η^1 - and η^2 -coordination of phosphaalkenes in Pt complexes, with a range of substituents dictating the bonding mode. ^{128,130}	20
Figure 8: Five postulated metallaphosphaalkene types	21
Figure 9: Bridging phosphaalkenyls demonstrating both σ -bonding and η^1 -coordination of the phosphorus centres to the Fe centres.	26
Figure 10: A diphosphaalkyne bridging two Pt complexes. ¹⁷¹	29
Figure 11: DFT-optimized structure of $[\text{RuCl}(\text{CO})(\text{PPh}_3)_2(\text{P}=\text{CHSiMe}_3)]$ (2). H atoms omitted for clarity.	38
Figure 12: DFT-optimised structure of 2 showing the HOMO (left) and LUMO (right).	38
Figure 13: Molecular structure of one molecule of $[\text{RuCl}(\text{CO})(\text{PPh}_3)_2(\text{P}=\text{CHSiMe}_3)]$ (2), in crystals of Et_2O solvate. 50% thermal ellipsoids. H atoms omitted for clarity.	39
Figure 14: Structure of 5 in crystals of the DCM solvate. 50% thermal ellipsoids. H atoms and solvent molecules omitted for clarity.	41
Figure 15: Molecular structure of one molecule of 5 . 50% thermal ellipsoids. H atoms omitted for clarity.	41
Figure 16: Optimised structure of 5 calculated by DFT (B3LYP/6-31G**, LANL2DZ (Ru))	42
Figure 17: Two extremes of the Dewar–Chatt–Duncanson-type model, describing the nature of 5 and analogous compounds.	43
Figure 18: The previous sole example of an η^2 -ruthenaphosphaalkene. ²⁰⁹	44
Figure 19: General structure of compounds 6–9 .	45
Figure 20: $[\text{Ru}(\text{CO})\{\kappa^3\text{-}N,C,P\text{-P}(\text{Pz}^{\text{R}''})\text{CH}(\text{R})\}(\text{PPh}_3)_2]$ (10–14).	46
Figure 21: Two isomers synthesised upon addition of $\text{Li}(\text{mt})$ to 2 and 3 .	48
Figure 22: Proposed structure of complex type B , formed upon addition of MeLi or MeMgBr to complex 2 .	57
Figure 23: Proposed structures of complex type B given loss of Cl^- facilitated by (a) coordination of THF and (b) orthometallation.	59
Figure 24: Proposed structure for complex type C , formed upon reaction of 1 with HPz^*	61
Figure 25: Proposed structure of complex type E , formed upon addition of $\text{HPz}^{(\text{CF}_3)_2}$ to 2 .	63

- Figure 26: Hydridic proton resonances from the ^1H NMR spectrum of the crude product achieved *via* addition of $\text{HC}\equiv\text{CCO}_2\text{H}$ to **17**. 74
- Figure 27: Molecular structure for **22b**. 50% thermal ellipsoids. H atoms omitted for clarity. 79
- Figure 28: Selected phosphorus resonances from the $^{31}\text{P}\{^1\text{H}\}$ (161.7 MHz) NMR spectrum of **F-2** upon addition of 2 AgOTf to **20** with subsequent addition of 4 $\text{HC}\equiv\text{CCO}_2\text{Me}$, in CDCl_3 . 83
- Figure 29: Attempted synthesis of bis(alkynyl) complexes of the type $[\text{Ru}(\text{dppe})_2(\text{C}\equiv\text{CO}_2\text{R})_2]$. 86
- Figure 30: Molecular structure for **34**. H atoms omitted for clarity. 50% thermal ellipsoids. 103
- Figure 31: Plot of (A) HOMO, (B) HOMO-1, (C) LUMO, (D) HOMO-6 for **40**. 109
- Figure 32: Optimised structure of **45** obtained through DFT calculations (B3LYP/6-31G**, LANL2DZ (Ru)). 111
- Figure 33: Molecular structure of **45**. 50% thermal ellipsoids. H atoms omitted for clarity. 111
- Figure 34: Optimised structure of **40** obtained by DFT calculations (B3LYP/6-31G** for H,C,P,O; LANL2DZ for Ru) depicted as a space-fill model. 100% Van der Waals radii. 113

LIST OF SCHEMES

- Scheme 1: The first stable phosphorus $3p_{\pi}$ – $2p_{\pi}$ systems. *Reagents and Conditions*: (i) N^iPr_2Et , DMF, 0 °C. 1
- Scheme 2: Synthetic procedure for the synthesis of the first substituted phosphabenzene. *Reagents and Conditions*: (i) PBr_3 ; (ii) DBN. 2
- Scheme 3: Synthesis of a diphosphabenzene *via* a [2+2+2] cycloaddition. *Reagents and Conditions*: (i) $HC\equiv CR$, toluene, –30 °C; (ii) $4^tBuC\equiv P$, toluene, –30 °C, 3 h. 3
- Scheme 4: A hafnium triphosphabenzene complex synthesised *via* $^tBuC\equiv P$ trimerization. *Reagents and Conditions*: (i) $3^tBuC\equiv P$, 0 °C, 1 h. 3
- Scheme 5: Synthesis of a diphosphabenzene. *Reagents and Conditions*: (i) $RhCl_3$, MeOH, r.t.; (ii) hexane, reflux. 3
- Scheme 6: Friedel–Crafts acylation yielding a phospholide ligand. *Reagents and Conditions*: (i) xylene, 150 °C; (ii) CH_3COCl , $AlCl_3$, DCM, 25 °C. 6
- Scheme 7: Synthesis of the first coordinated 1,3-phosphabutadiene compound. *Reagents and Conditions*: (i) $2^tBuC\equiv P$. 7
- Scheme 8 Reaction of $[CpRh(P_2C_2^tBu_2)]$ with $[Rh_2Cl_2(C_2H_4)_4]$. 8
- Scheme 9: Synthesis of $\eta^1:\eta^4$ -diphosphacyclobutadiene sandwich complexes. *Reagents and Conditions*: (i) $4RC\equiv P$, THF, 16 h, r.t.; (ii) $AuCl(PPh_3)$, AgCl or $AgSbF_6$, PMe_3 , THF, 16 h, –78 °C ($R = Ad$, tPent ; $R' = PMe_3$; $M = Au$, Ag). 8
- Scheme 10: Becker's phosphalkene synthesis 9
- Scheme 11: Formation of an unstable phosphacumulene ($R = Ph$, tBu , C_2H_5 , Mes). 10
- Scheme 12: 1,3-silatropic migration leading to a phosphalkene–phosphine. *Reagents and Conditions*: (i) pentane, 6 h, 0 °C. 12
- Scheme 13: Synthesis of a $Mes^*P=CHX$ *via* double dehydrohalogenation. *Reagents and Conditions*: (i) KOH, THF, 24 h. 13
- Scheme 14: Synthesis of a phosphalkene *via* an adapted Peterson Olefination reaction. *Reagents and Conditions*: (i) nBuLi , THF; (ii) $ClSiMe_2^tBu$; (iii) PhCHO. 14
- Scheme 15: Phosphalkene synthesis *via* a tantalum phosphinidene. An adaptation of the Wittig reaction. *Reagents and Conditions*: (i) DCM, 7 h, 95 °C. 15
- Scheme 16: 'Phospha-Wittig' reaction to form phosphalkenes ($X = H$, Cl, NO_2 , OMe, NMe_2 ; Ar = dmp, Mes*). *Reagents and Conditions*: (i) THF. 15
- Scheme 17: Phospha-Wittig reaction yielding an η^1 -coordinated phosphalkene ($R = Ph$, Me; R. *Reagents and Conditions*: (i) nBuLi , THF, –70 °C; (ii) $R'_2C=O$, DBO, $C_6H_6:C_5H_{12}$ (1:2). 17
- Scheme 18: Synthesis of an η^1 -coordinated phosphalkene *via* an oxaphosphirane. *Reagents and Conditions*: (i) $[TiCpCl_3]/Zn$, THF, 16 h, r.t. 18

Scheme 19: Synthesis of the first C-metallaphosphaalkene. <i>Reagents and Conditions</i> : (i) LiP(SiMe ₃) ^t Bu, Et ₂ O, -78 °C; (ii) 20 °C, 30 min. ¹⁴⁰	22
Scheme 20: Synthesis of C-mercuriophosphaalkenes <i>via</i> a C-lithiophosphaalkene. <i>Reagents and Conditions</i> : (i) ⁿ BuLi, THF, 30 min, -80 °C; (ii) HgCl ₂ ; (iii) ½ HgCl ₂ .	23
Scheme 21: Heterocyclic C-metallated phosphaaalkenes <i>via</i> an η ² -coordinated phosphaaalkyne. <i>Reagents and Conditions</i> : (i) BEt ₃ ; (ii) R ¹ C≡CR ² (R ¹ /R ² ≠ SiR ₃). ¹³⁸	24
Scheme 22: Heterocyclic compounds incorporating the C=P moiety, formed within the coordination sphere of the Ti centre (R = Ad, ^t Bu). <i>Reagents and Conditions</i> : (i) 2 RC≡P, pentane, 2 h. ¹⁴⁷	24
Scheme 23: Phosphaalkyne-imido [2+2] cycloaddition furnishing a C-metallaphosphaalkene. <i>Reagents and Conditions</i> : (i) ^t BuC≡P, C ₆ H ₆ , 48 h, r.t. ¹⁴⁸	25
Scheme 24: A P-metallaphosphaalkene with the P=C bond formed within the coordination sphere of iron. <i>Reagents and Conditions</i> : (i) ^t BuCOCl, THF, 35 °C, 1 h.	25
Scheme 25: Hydro-ruthenation yielding an η ¹ -P-metallophosphaalkene with subsequent electrophilic addition at the phosphorus centre.	27
Scheme 26: First examples of η ¹ -coordinated phosphaaalkyne compounds. ¹⁷²	30
Scheme 27: First example of the cyaphide ligand formed <i>in situ</i> . <i>Reagents and Conditions</i> : (i) Pd(PEt ₄), C ₆ H ₆ , 8 h, r.t.; (ii) Pt(PEt ₄), C ₆ H ₆ , 30 min, r.t.	31
Scheme 28: Synthesis of the first η ² :η ¹ -coordination compound of a phosphaaalkyne. <i>Reagents and Conditions</i> : (i) [Mo(CO) ₅ ·(THF)], THF, 12 h, r.t. ¹⁸²	32
Scheme 29: Synthesis of the first polyphosphole <i>via</i> copper-catalysed cross-coupling. <i>Reagents and Conditions</i> : (i) ⁿ BuLi, THF, -90 °C; (ii) CuCl ₂ , -90 °C, 1 h; (iii) 25 °C, 2 h. ¹⁸⁹	33
Scheme 30: Synthesis of poly(<i>p</i> -phenylenephosphaalkene) <i>via</i> the Becker condensation. <i>Reagents and Conditions</i> : (i) 85 °C, 8 h. ^{190,191}	33
Scheme 31: The Phospha-Wittig reaction used to furnish an extended π-system incorporating P=C (R = Ph, 2,6-Cl ₂ C ₆ H ₃). <i>Reagents and Conditions</i> : (i) Zn, PMe ₃ , ArC(H)O, THF, 2 h. ¹⁹⁶	34
Scheme 32: Synthesis of 2 and 3 <i>via</i> the phosphaaalkynes P≡CSiMe ₂ R (R = Me, Ph). <i>Reagents and Conditions</i> : (i) Mg, Et ₂ O, PCl ₃ , 16 h, -78 °C; (ii) AgOTf, DABCO, toluene, 1 h, r.t.; (iii) DCM, 1 h, r.t.	37
Scheme 33: Synthesis of complexes 4 and 5 . <i>Reagents and Conditions</i> : (i) ⁿ BuLi, THF, 10 min, r.t.; (ii) THF, 1 h, r.t.	40
Scheme 34: Possible mechanisms for the formation of complexes 4–16 <i>via</i> (i) initial coordination of the pyrazolyl ring to the ruthenium centre and (ii) initial nucleophilic attack at the phosphaaalkenic phosphorus centre.	51
Scheme 35: Electrophilic attack at the P=C phosphorus centre of 1 ²¹¹	55
Scheme 36: Reaction of 2 and 3 with LiNu yielding a complex of type A	55

Scheme 37: Scheme showing the possible mechanism for the synthesis of compounds 4–16 based on mechanistic studies.	64
Scheme 38: Schematic showing alkyne/vinylidene tautomerisation demonstrating the two potential pathways, A and B , leading to a metal-vinylidene complex.	67
Scheme 39: Formation of a metal-alkynyl <i>via</i> a stable vinylidene intermediate	68
Scheme 40: Formation of Group 6 propargylidyne complexes stabilised by Tp' ligands ²⁶³	70
Scheme 41: Generic scheme of a Sonogashira cross-coupling reaction catalysed by a Pd ⁰ complex and CuX.	71
Scheme 42: Installation of a functional group at the terminus of a propargylidyne ligand <i>via</i> a gold cross-coupling reaction. <i>Reagents and Conditions</i> : (i) [Co ₃ (μ ₃ -CBr)(μ-dppm)(CO) ₇], Pd(PPh ₃) ₄ , CuI, THF, 2 h, r.t.	72
Scheme 43: Attempted synthesis of [RuH(CO) ₂ (PPh ₃) ₂ (C≡CCO ₂ H)] yielding the known complex 18 . <i>Reagents and Conditions</i> : (i) 2 HC≡CCO ₂ H, THF, 1 h, r.t.	74
Scheme 44: Optimised pathway for the formation of [Ru]–CCH, leading to formation of [Ru]=C=CH upon protonation, calculated using DFT ([Ru] = CpRu(dmpe)). ²⁸²	75
Scheme 45: Attempted synthesis of [RuH(CO)(PPh ₃) ₂ (C≡CCH ₂ Cl)], yielding compounds 18 and 19 . <i>Reagents and Conditions</i> : (i) 2 HC≡CCH ₂ Cl, THF, 1 h, r.t.	76
Scheme 46: General scheme for the formation of an allenyl product upon addition of a propargyl halide to 17 .	77
Scheme 47: Synthesis of 22a and 22b ; <i>Reagents and Conditions</i> : (i) 2 HC≡CCO ₂ Me, DCM, 16 h, r.t.; (ii) 2 KO ^t Bu, MeOH, r.t.	78
Scheme 48: Synthesis of compounds 22–27(a–c) ; <i>Reagents and Conditions</i> : (i) DCM, 16 h, r.t.; (ii) DCM, MeOH, r.t.; (iii) xs. KO ^t Bu, DCM, MeOH, 16 h, r.t.	81
Scheme 49: Attempted synthesis of [RuCl(dppe) ₂ (C≡CC(OSiMe ₃)=P(OSiMe ₃))] by addition of P(TMS) ₃ to 22a , leading to the synthesis of a new unknown species. <i>Reagents and Conditions</i> : (i) P(TMS) ₃ , THF, 2 h, r.t.	88
Scheme 50: Attempted synthesis of compounds [M(≡CC≡CCO ₂ Me){OC(O)CF ₃ }(CO) ₂ (tmeda)] (M = W and Mo). <i>Reagents and Conditions</i> : (i) LiC≡CCO ₂ Me; (ii) (CF ₃ CO) ₂ O; (iii) tmeda.	89
Scheme 51: Attempted synthesis of compounds [Tp*W(CO)(≡CC≡CCO ₂ Me)] and [Tp*Mo(CO)(≡CC≡CCO ₂ Et)].	91
Scheme 52: Synthesis of compounds [Tp'M(CO) ₂ (≡CC≡C(C ₆ H ₄)CO ₂ Me)] (Tp' = Tp and M = W and Mo; Tp' = Tp* and M = W and Mo) under reaction conditions I–XVIII .	92
Scheme 53: Coupling reaction to synthesise [TpW(CO) ₂ (≡CC≡C(C ₆ H ₄)CO ₂ Me)]. <i>Reagents and Conditions</i> : (i) I(C ₆ H ₄)CO ₂ Me, Pd(PPh ₃) ₄ , CuI, THF.	97
Scheme 54: Synthesis of the first stable cyaphide compound.	99
Scheme 55: Proposed mechanism of cyaphide formation (R = Ph) upon addition of NaOPh, with formation of an intermediate species observed by ³¹ P{ ¹ H} NMR spectroscopy. ³⁰⁸	100

Scheme 56: Synthesis of complexes **34–39**. *Reagents and Conditions*: (i) AgOTf, DCM, 5 min, r.t.; (ii) TMS-C≡P, toluene, 1 h, r.t. 102

Scheme 57: Synthesis of compounds **40–45**. *Reagents and Conditions*: (i) KO^tBu, THF, 1 h, r.t. 105

Scheme 58: Proposed structure of compound **G** (R = Ph), formed upon addition of KO^tBu in MeOH to **34**. *Reagents and Conditions*: (i) KO^tBu, MeOH, DCM, 1h, r.t. 108

LIST OF TABLES

Table 1: Selected bond lengths (Å) and angles (°) for the X-ray and DFT optimised structures for compound 2 .	39
Table 2: Selected bond lengths (Å) and angles (°) for 5 .	42
Table 3: Selected $^{31}\text{P}\{^1\text{H}\}$, $^{13}\text{C}\{^1\text{H}\}$ and ^1H NMR chemical shifts (ppm) of 4–9 in CD_2Cl_2	45
Table 4: Selected $^{31}\text{P}\{^1\text{H}\}$, $^{13}\text{C}\{^1\text{H}\}$, ^1H NMR and ^{19}F NMR chemical shifts (ppm) for complexes 10–14 in CDCl_3	47
Table 5: Selected $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR (ppm) and spin–spin couplings (Hz) for both isomers of compounds 15 and 16 in CD_2Cl_2	50
Table 6: Selected $^{31}\text{P}\{^1\text{H}\}$, $^{13}\text{C}\{^1\text{H}\}$ and ^1H NMR chemical shifts (ppm) for complexes of type A(1–4) in CDCl_3	53
Table 7: Selected $^{31}\text{P}\{^1\text{H}\}$ resonances (ppm) and $^2J_{\text{PP}}$ couplings (Hz) for compound of type A formed upon addition of MeLi or MeMgBr 2 or 3 in CDCl_3	54
Table 8: Selected $^{31}\text{P}\{^1\text{H}\}$, $^{13}\text{C}\{^1\text{H}\}$, ^1H NMR and ^{29}Si NMR chemical shifts (ppm) for compound type B-1 upon addition of MeLi to 2 .	56
Table 9: Selected $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR data for compounds B-1–B-4 upon addition of MeLi or MeMgBr to 2 and 3 in CDCl_3	58
Table 10: Selected $^{31}\text{P}\{^1\text{H}\}$, $^{13}\text{C}\{^1\text{H}\}$ and ^1H NMR NMR chemical shifts (ppm) and spin–spin couplings (Hz) for compounds C-1 and D-1 , formed upon reaction of HPz* with 1 in CDCl_3	60
Table 11: Selected bond lengths (Å) and angles (°) for 22b .	79
Table 12: Selected $^{31}\text{P}\{^1\text{H}\}$, ^1H NMR NMR data (ppm) and J -couplings (Hz) for vinylidene (a), alkyne (b) and hydride (c) compounds 22–27 (Scheme 47) in CDCl_3 . [‡]	81
Table 13: $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopic data for unknown species F-1 and F-2 upon addition of $\text{HC}\equiv\text{CCO}_2\text{Me}$ and $\text{HC}\equiv\text{CCO}_2\text{Et}$ to 20 , respectively, in CDCl_3	83
Table 14: Variations of Sonogashira Coupling Reactions Attempted with compounds 29–32 (Scheme 51) and $\text{IC}_6\text{H}_4\text{CO}_2\text{R}$	93
Table 15: Selected Bond Lengths (Å) and Angles (°) for 34	103
Table 16: Selected $^{31}\text{P}\{^1\text{H}\}$ and $^{13}\text{C}\{^1\text{H}\}$ NMR shifts (ppm) and IR stretches (cm^{-1}) for complexes of the type $[\text{Ru}(\text{dppe})_2(\text{TMSC}\equiv\text{P})(\text{C}\equiv\text{CR})][\text{OTf}]$ (in CDCl_3) and $[\text{Ru}(\text{dppe})_2(\text{C}\equiv\text{P})(\text{C}\equiv\text{CR})]$ (in CD_2Cl_2)	104
Table 17: Selected bond lengths (Å) and angles (°) for 40 , obtained by DFT calculations (B3LYP/6-31G** for H,C,P,O; LANL2DZ for Ru).	110
Table 18: Selected bond lengths (Å) and angles (°) for 45 , obtained by both X-ray diffraction studies and DFT calculations (B3LYP/6-31G** for H,C,P,O; LANL2DZ for Ru).	112

LIST OF COMPOUNDS

1	$[\text{RuCl}(\text{CO})(\text{PPh}_3)_2(\text{P}=\text{CH}^t\text{Bu})]$
2	$[\text{RuCl}(\text{CO})(\text{PPh}_3)_2(\text{P}=\text{CHSiMe}_3)]$
3	$[\text{RuCl}(\text{CO})(\text{PPh}_3)_2(\text{P}=\text{CHSiMe}_2\text{Ph})]$
4	$[\text{Ru}(\text{CO})\{\kappa^3\text{-}N,C,P\text{-P}(\text{Pz}^*)\text{CH}(\text{SiMe}_3)\}(\text{PPh}_3)_2]$
5	$[\text{Ru}(\text{CO})\{\kappa^3\text{-}N,C,P\text{-P}(\text{Pz})\text{CH}(\text{SiMe}_3)\}(\text{PPh}_3)_2]$
6	$[\text{Ru}(\text{CO})\{\kappa^3\text{-}N,C,P\text{-P}(\text{Pz}^*)\text{CH}(\text{SiMe}_2\text{Ph})\}(\text{PPh}_3)_2]$
7	$[\text{Ru}(\text{CO})\{\kappa^3\text{-}N,C,P\text{-P}(\text{Pz})\text{CH}(\text{SiMe}_2\text{Ph})\}(\text{PPh}_3)_2]$
8	$[\text{Ru}(\text{CO})\{\kappa^3\text{-}N,C,P\text{-P}(\text{Pz}^*)\text{CH}(^t\text{Bu})\}(\text{PPh}_3)_2]$
9	$[\text{Ru}(\text{CO})\{\kappa^3\text{-}N,C,P\text{-P}(\text{Pz})\text{CH}(^t\text{Bu})\}(\text{PPh}_3)_2]$
10	$[\text{Ru}(\text{CO})\{\kappa^3\text{-}N,C,P\text{-P}(\text{Pz}^{t\text{Bu}})\text{CH}(\text{SiMe}_3)\}(\text{PPh}_3)_2]$
11	$[\text{Ru}(\text{CO})\{\kappa^3\text{-}N,C,P\text{-P}(\text{Pz}^{\text{Me,CF}_3})\text{CH}(\text{SiMe}_3)\}(\text{PPh}_3)_2]$
12	$[\text{Ru}(\text{CO})\{\kappa^3\text{-}N,C,P\text{-P}(\text{Pz}^{\text{CF}_3})\text{CH}(\text{SiMe}_3)\}(\text{PPh}_3)_2]$
13	$[\text{Ru}(\text{CO})\{\kappa^3\text{-}N,C,P\text{-P}(\text{Pz}^{\text{Me,CF}_3})\text{CH}(\text{SiMe}_2\text{Ph})\}(\text{PPh}_3)_2]$
14	$[\text{Ru}(\text{CO})\{\kappa^3\text{-}N,C,P\text{-P}(\text{Pz}^{\text{CF}_3})\text{CH}(\text{SiMe}_2\text{Ph})\}(\text{PPh}_3)_2]$
Ru-N-15	$[\text{Ru}(\text{CO})\{\kappa^3\text{-}N,P,C\text{-P}(N\text{-mt})\text{CH}(\text{SiMe}_3)\}(\text{PPh}_3)_2]$
Ru-S-15	$[\text{Ru}(\text{CO})\{\kappa^3\text{-}S,P,C\text{-P}(S\text{-mt})\text{CH}(\text{SiMe}_3)\}(\text{PPh}_3)_2]$
Ru-N-16	$[\text{Ru}(\text{CO})\{\kappa^3\text{-}N,P,C\text{-P}(N\text{-mt})\text{CH}(\text{SiMe}_2\text{Ph})\}(\text{PPh}_3)_2]$
Ru-S-16	$[\text{Ru}(\text{CO})\{\kappa^3\text{-}S,P,C\text{-P}(S\text{-mt})\text{CH}(\text{SiMe}_2\text{Ph})\}(\text{PPh}_3)_2]$
17	$[\text{Ru}(\text{CO})_2(\text{PPh}_3)_3]$
18	$[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$
19	$[\text{RuCl}(\text{CO})_2(\text{PPh}_3)_2(\text{CH}=\text{C}=\text{CH}_2)]$
20	$[\text{RuCl}_2(\text{dppe})_2]$
21	$[\text{RuCl}(\text{dppe})_2][\text{OTf}]$
22a	$[\text{RuCl}(\text{dppe})_2(\text{C}=\text{CHCO}_2\text{Me})][\text{OTf}]$
22b	$[\text{RuCl}(\text{dppe})_2(\text{C}\equiv\text{CCO}_2\text{Me})]$
22c	$[\text{RuH}(\text{dppe})_2(\text{C}\equiv\text{CCO}_2\text{Me})]$
23a	$[\text{RuCl}(\text{dppe})_2(\text{C}=\text{CHCO}_2\text{Et})][\text{OTf}]$
23b	$[\text{RuCl}(\text{dppe})_2(\text{C}\equiv\text{CCO}_2\text{Et})]$
23c	$[\text{RuH}(\text{dppe})_2(\text{C}\equiv\text{CCO}_2\text{Et})]$
24a	$[\text{RuCl}(\text{dppe})_2(\text{C}=\text{CHPh})][\text{OTf}]$
24b	$[\text{RuCl}(\text{dppe})_2(\text{C}\equiv\text{CPh})]$
24c	$[\text{RuH}(\text{dppe})_2(\text{C}\equiv\text{CPh})]$
25a	$[\text{RuCl}(\text{dppe})_2(\text{C}=\text{CHC}_6\text{H}_4\text{CO}_2\text{Me})][\text{OTf}]$

25b	$[\text{RuCl}(\text{dppe})_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{CO}_2\text{Me})]$
25c	$[\text{RuH}(\text{dppe})_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{CO}_2\text{Me})]$
26a	$[\text{RuCl}(\text{dppe})_2(\text{C}=\text{CHC}_6\text{H}_4\text{CO}_2\text{Et})][\text{OTf}]$
26b	$[\text{RuCl}(\text{dppe})_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{CO}_2\text{Et})]$
26c	$[\text{RuH}(\text{dppe})_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{CO}_2\text{Et})]$
27a	$[\text{RuCl}(\text{dppe})_2(\text{C}=\text{CHC}_6\text{H}_4\text{OMe})][\text{OTf}]$
27b	$[\text{RuCl}(\text{dppe})_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{OMe})]$
27c	$[\text{RuH}(\text{dppe})_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{OMe})]$
28a	$[\text{RuCl}(\text{dppe})_2(\text{C}=\text{CHCH}_2\text{Cl})][\text{OTf}]$
28b	$[\text{RuCl}(\text{dppe})_2(\text{C}\equiv\text{CCH}_2\text{Cl})]$
28c	$[\text{RuH}(\text{dppe})_2(\text{C}\equiv\text{CCH}_2\text{Cl})]$
29	$[\text{TpW}(\text{CO})_2(\equiv\text{CC}\equiv\text{CSiMe}_3)]$
30	$[\text{TpMo}(\text{CO})_2(\equiv\text{CC}\equiv\text{CSiMe}_3)]$
31	$[\text{Tp}^*\text{W}(\text{CO})_2(\equiv\text{CC}\equiv\text{CSiMe}_3)]$
32	$[\text{Tp}^*\text{Mo}(\text{CO})_2(\equiv\text{CC}\equiv\text{CSiMe}_3)]$
33	$[\text{TpW}(\text{CO})_2(\equiv\text{CC}\equiv\text{CAuPPh}_3)]$
34	$[\text{Ru}(\text{dppe})_2(\text{C}\equiv\text{CCO}_2\text{Me})(\text{P}\equiv\text{CSiMe}_3)][\text{OTf}]$
35	$[\text{Ru}(\text{dppe})_2(\text{C}\equiv\text{CCO}_2\text{Et})(\text{P}\equiv\text{CSiMe}_3)][\text{OTf}]$
36	$[\text{Ru}(\text{dppe})_2(\text{C}\equiv\text{CPh})(\text{P}\equiv\text{CSiMe}_3)][\text{OTf}]$
37	$[\text{Ru}(\text{dppe})_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{CO}_2\text{Me})(\text{P}\equiv\text{CSiMe}_3)][\text{OTf}]$
38	$[\text{Ru}(\text{dppe})_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{CO}_2\text{Et})(\text{P}\equiv\text{CSiMe}_3)][\text{OTf}]$
39	$[\text{Ru}(\text{dppe})_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{OMe})(\text{P}\equiv\text{CSiMe}_3)][\text{OTf}]$
40	$[\text{Ru}(\text{dppe})_2(\text{C}\equiv\text{CCO}_2\text{Me})(\text{C}\equiv\text{P})]$
41	$[\text{Ru}(\text{dppe})_2(\text{C}\equiv\text{CCO}_2\text{Et})(\text{C}\equiv\text{P})]$
42	$[\text{Ru}(\text{dppe})_2(\text{C}\equiv\text{CPh})(\text{C}\equiv\text{P})]$
43	$[\text{Ru}(\text{dppe})_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{CO}_2\text{Me})(\text{C}\equiv\text{P})]$
44	$[\text{Ru}(\text{dppe})_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{CO}_2\text{Et})(\text{C}\equiv\text{P})]$
45	$[\text{Ru}(\text{dppe})_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{OMe})(\text{C}\equiv\text{P})]$

What can be the ‘why’ for these happenings?

—*Peyton Rous, Nobel Laureate, 1966*

ACKNOWLEDGEMENTS	II
SUMMARY	III
ABBREVIATIONS	IV
LIST OF FIGURES	V
LIST OF SCHEMES	VII
LIST OF TABLES	XI
LIST OF COMPOUNDS	XII
CHAPTER 1: INTRODUCTION	1
1.1 A Brief History of Low-Coordinate Phosphorus	1
1.1.1 <i>Phosphabenzenes</i>	2
1.1.2 <i>Phospholides</i>	4
1.1.3 <i>Diphosphacyclobutadienes</i>	7
1.1.4 <i>Phosphaalkenes and Phosphaalkynes</i>	9
1.1.5 <i>Phosphacumulenes</i>	10
1.2 Phosphaalkenes	11
1.2.1 <i>Synthesis and properties of organo-phosphaalkenes</i>	11
1.2.2 <i>Coordination Chemistry of Phosphaalkenes</i>	16
1.2.3 <i>Metallaphosphaalkenes</i>	21
1.3 Phosphaalkynes	28
1.3.1 <i>Synthesis of Organo-phosphaalkynes</i>	28
1.3.2 <i>Coordination compounds of phosphaalkynes</i>	28
1.4 Extended Conjugation in Low-Coordinate Phosphorus-Containing Molecules	32
1.5 Concluding Remarks	34
CHAPTER 2: INVESTIGATION INTO THE STRUCTURAL AND ELECTRONIC PROPERTIES OF RUTHENA-PHOSPHAALKENES AND THEIR CHEMISTRY	36
2.1 Introduction	36
2.2 Synthesis and Structure of $[\text{Ru}(\text{CO})\{\kappa^3\text{-N,C,P-P}(\text{Pz}')\text{CH(R)}\}(\text{PPh}_3)_2]$	37
2.2.1 <i>Synthesis of $[\text{RuCl}(\text{CO})(\text{PPh}_3)_2(\text{P=CHR})]$ ($\text{R} = \text{SiMe}_3$ (2), SiMe_2Ph (3))</i>	37
2.2.2 <i>Synthesis and Characterisation of $[\text{Ru}(\text{CO})\{\kappa^3\text{-N,C,P-P}(\text{Pz}^*)\text{CH}(\text{SiMe}_3)\}(\text{PPh}_3)_2]$</i>	40
2.2.3 <i>Structural Features of Complexes 4 and 5</i>	40
2.2.4 <i>Synthesis, Structure and Properties of $[\text{Ru}(\text{CO})\{\kappa^3\text{-N,C,P-P}(\text{Pz}')\text{CH(R)}\}(\text{PPh}_3)_2]$ ($\text{R} = \text{SiMe}_2\text{Ph}$, $t\text{Bu}$)</i>	44
2.3 Synthesis and Properties of $[\text{Ru}(\text{CO})\{\kappa^3\text{-N,C,P-P}(\text{Pz}^{\text{R/R'}})\text{CH(R)}\}(\text{PPh}_3)_2]$	46
2.4 Synthesis and Properties of Complexes of the Type $[\text{Ru}(\text{CO})\{\kappa^3\text{-N,P,C-P(mt)}\text{CH(R)}\}(\text{PPh}_3)_2]$	47
2.5 Mechanistic Studies	50
2.5.1 <i>Reactions of $[\text{RuCl}(\text{CO})(\text{PPh}_3)_2(\text{P=CHSiMe}_2\text{R})]$ ($\text{R} = \text{Me}$ (2), Ph (3)) with Nitrogen- and Carbon-based Nucleophiles</i>	50

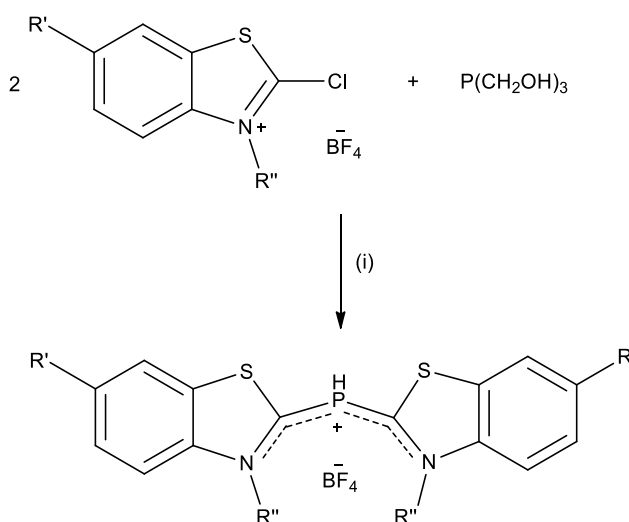
2.5.2	<i>Structural Features of Complexes of Type A</i>	54
2.5.3	<i>Additional Reactions of Carbon-Based Nucleophiles [RuCl(CO)(PPh₃)₂(P=CHSiMe₂R)] (R = Me (2), Ph (3))</i>	56
2.5.4	<i>Reactions of HPz* with Complexes [RuCl(CO)(PPh₃)₂(P=CHR)] (R = ^tBu (1), SiMe₃ (2), SiMe₂Ph (3))</i>	59
2.5.5	<i>Summary of mechanistic studies and their implications</i>	63
2.6	<i>Concluding Remarks</i>	64
CHAPTER 3: TRANSITION METAL VINYLIDENE, ALKYNYL AND PROPARGYLIDYNE COMPLEXES AS POTENTIAL ALKYNYL–PHOSPHAALKYNE PRECURSORS		66
3.1	<i>Introduction</i>	66
3.1.1	<i>Organometallic polyacetylenes</i>	66
3.1.2	<i>Vinylidene/Alkyne Tautomerisation</i>	67
3.1.3	<i>Alkynyl–Carbyne Complexes</i>	69
3.2	<i>Results and Discussion</i>	73
3.2.1	<i>Synthesis of Ru^{II}–Alkynyl Complexes</i>	73
3.2.2	<i>Synthesis of propargylidyne complexes</i>	88
3.3	<i>Concluding Remarks</i>	97
CHAPTER 4: THE SYNTHESIS AND STRUCTURE OF RUTHENIUM CYAPHIDE COMPLEXES		99
4.1	<i>Introduction</i>	99
4.2	<i>Synthesis and Structure of Ruthenium η¹-Phosphaalkyne Complexes [Ru(dppe)₂(C≡CR)(η¹-P≡CSiMe₃)]</i>	101
4.2.1	<i>Synthesis and Characterisation</i>	101
4.2.2	<i>Structural properties of 34</i>	102
4.2	<i>Synthesis of ruthenium cyaphides [Ru(dppe)₂(C≡CR)(C≡P)]</i>	105
4.2.1	<i>Synthesis and Characterisation</i>	105
4.2.2	<i>Electronic and Structural Properties of Complexes 40–45</i>	108
4.2.3	<i>Chemical Properties and Reactivity Cyaphide-Containing Compounds</i>	112
4.3	<i>Concluding Remarks</i>	115
CHAPTER 5: EXPERIMENTAL		116
5.1	<i>General Experimental Details</i>	116
5.2	<i>Experimental Details For Chapter 2</i>	117
5.2.1	<i>Synthesis of Compounds 2–16</i>	117
5.2.2	<i>Addition of N- and C-donor nucleophiles to compounds 2 and 3, synthesising Compounds of Type A</i>	123
5.2.3	<i>Addition of C-donor nucleophiles to compounds 2 and 3, synthesising compounds of type B</i>	125
5.2.4	<i>Addition of HPz' to compounds 1, 2 and 3, synthesising compounds of types C, D and E</i>	126
5.3	<i>Experimental Details For Chapter 3</i>	128

5.3.1	<i>Attempted synthesis of compounds of the type $[\text{RuH}(\text{CO})_2(\text{PPh}_3)_2(\text{C}\equiv\text{CR})]$ ($\text{R} = \text{CO}_2\text{H}, \text{CH}_2\text{Cl}$)</i>	128
5.3.2	<i>Synthesis of Complexes 22–27(a,b,c)</i>	129
5.3.3	<i>Attempted Synthesis of Bis(Alkynyl) Complexes</i>	135
5.3.4	<i>Attempted Installation of phosphalkene termini</i>	137
5.3.5	<i>Attempted synthesis of tungsten and molybdenum propargylidyne complexes terminating in CO_2Me and SiMe_3</i>	138
5.3.6	<i>Cross-Coupling reactions</i>	142
5.4	<i>Experimental Details For Chapter 4</i>	146
5.4.1	<i>Synthesis of Complexes η^1-Phosphaalkyne Complexes 34–39</i>	146
5.4.2	<i>Synthesis of Terminal Cyaphide Complexes 40–45</i>	149
5.4.3	<i>Reactivity studies with compounds 40–45</i>	151
	REFERENCES	154
	APPENDIX	164

CHAPTER 1: INTRODUCTION

1.1 A BRIEF HISTORY OF LOW-COORDINATE PHOSPHORUS

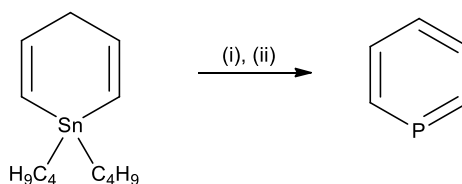
The chemistry of low-coordinate phosphorus has long been an area of interest for chemists and has found application in many fields including organic synthesis, catalysis, organometallic chemistry and polymer chemistry. Historically, it had been a widely held belief that elements beyond the second row of the periodic table were able to form only very weak multiple bonds, as the longer σ -bonds associated with heavier elements should lead to poor π -orbital overlap resulting in weak p_π - p_π bonding.¹ However, in the 1960s such theoretical observations were challenged due to the pioneering work of Gier,² in which the $\text{HC}\equiv\text{P}$ molecule was synthesised by passing PH_3 through a rotating arc between graphite electrodes. Despite the highly pyrophoric nature of $\text{HC}\equiv\text{P}$ and its propensity to oligomerize, even at temperatures as low as $-130\text{ }^\circ\text{C}$, such an intriguing molecule sparked the curiosity of researchers. Three years later, Dimroth *et al.*³ prepared a phosphamethine-cyanin compound (Scheme 1), demonstrating for the first time a phosphorus-carbon $3p_\pi$ - $2p_\pi$ system, with a resonance assigned to the phosphorus centre at $\delta_\text{P} -26$ in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum.⁴ However, the ramifications of these seminal works would not become apparent for a number of years as interest in such compounds developed slowly.



Scheme 1: The first stable phosphorus $3p_\pi$ - $2p_\pi$ systems. *Reagents and Conditions:* (i) $\text{N}^i\text{Pr}_2\text{Et}$, DMF, $0\text{ }^\circ\text{C}$.

1.1.1 PHOSPHABENZENES

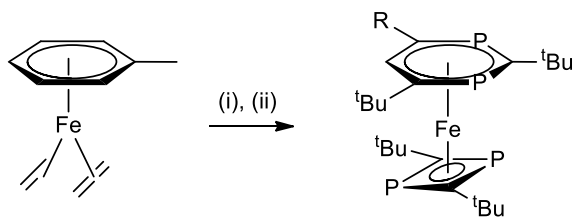
Following the publication of Dimroth's resonance-stabilised structures, Märkl synthesised the first phosphabenzene derivative, 2,4,6-triphenylphosphabenzene, upon addition of phenylphosphine to 2,4,6-triphenylpyrylium tetrafluoroborate,⁵⁻⁷ with a phosphorus resonance at δ_P 178 observed in the ^{31}P NMR spectrum. This represented a landmark in phosphorus chemistry, with a significant body of work in the field of aromatic low-coordinate phosphorus having since been established. Shortly thereafter, the parent phosphabenzene $\text{C}_5\text{H}_5\text{P}$ was isolated upon addition of the heterocyclic tin complex 1,4-dihydro-1,1-dibutylstanabenzene to PBr_3 and subsequent treatment with DBN (Scheme 2);⁸ the IUPAC term 'phosphinine' was later coined to describe the $\text{C}_5\text{H}_5\text{P}$ moiety. Since these seminal works, synthetic protocols have been established that allow access to a plethora of substituted phosphinines, with the most common methods being thermally induced aromatization from phosphacyclohexanones⁹⁻¹¹ and [4+2] cycloaddition reactions of either a phosphadiene/alkyne or a diene/phosphaalkyne.¹²⁻¹⁴



Scheme 2: Synthetic procedure for the synthesis of the first substituted phosphabenzene.

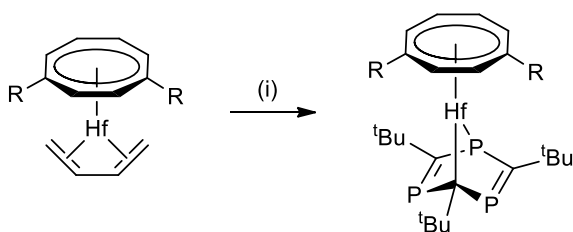
Reagents and Conditions: (i) PBr_3 ; (ii) DBN.

In addition to the traditional phosphinines, di- and tri-phosphabenzenes have also been developed, predominantly through trimerization of phosphaalkynes within the coordination sphere of a metal, with early examples including those of Cowley,¹⁵ Zenneck¹⁶ and Binger.^{17,18} Cowley and co-workers found that upon addition of $^t\text{BuC}\equiv\text{P}$ to the Mo complex $[(\eta^6\text{-C}_7\text{H}_8)\text{Mo}(\text{CO})_3]$, cycloheptatriene was replaced by the triphosphabenzene ligand 1,3,5-tri-tertbutyl-phosphabenzene. Some years later, Zenneck found that addition of $\text{HC}\equiv\text{CR}$ and 4 equivalents of $^t\text{BuC}\equiv\text{P}$ to the iron complex $[(\eta^6\text{-tol})\text{Fe}(\text{C}_2\text{H}_4)_2]$ furnished a novel sandwich complex with a 1,3-di-tertbutyl-5-methyl-diphosphabenzene ligand *via* a [2+2+2] cycloaddition (Scheme 3).



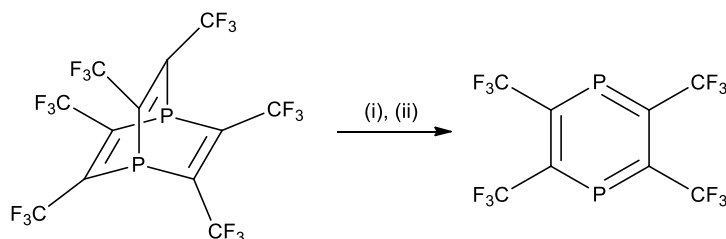
Scheme 3: Synthesis of a diphoshabenzene *via* a [2+2+2] cycloaddition. *Reagents and Conditions:* (i) $\text{HC}\equiv\text{CR}$, toluene, $-30\text{ }^{\circ}\text{C}$; (ii) $4\text{ }^t\text{BuC}\equiv\text{P}$, toluene, $-30\text{ }^{\circ}\text{C}$, 3 h.

Shortly thereafter, Binger reported the hafnium triphoshabenzene complex $(\eta^8\text{-C}_8\text{H}_6\text{R}_2)\text{Hf}(\text{C}_3^t\text{Bu}_3\text{P}_3)$ upon addition of $^t\text{BuC}\equiv\text{P}$ to $[(\eta^8\text{-C}_8\text{H}_6\text{R}_2)\text{Hf}(\text{C}_4\text{H}_6)]$ ($\text{R} = \text{H}, \text{SiMe}_3$) (Scheme 4). Since this time, Cloke and co-workers have reported the formation of phosphabenzenes within the coordination sphere of scandium from $^t\text{BuC}\equiv\text{P}$ *via* metal vapour synthesis, furnishing the triple-decker Sc^{I} complex $[\{\eta^5\text{-P}_3\text{C}_2^t\text{Bu}_2\}\text{Sc}]_2(\mu\text{-}\eta^6\text{:}\eta^6\text{-P}_3\text{C}_3^t\text{Bu}_3)$.¹⁹



Scheme 4: A hafnium triphoshabenzene complex synthesised *via* $^t\text{BuC}\equiv\text{P}$ trimerization. *Reagents and Conditions:* (i) $3\text{ }^t\text{BuC}\equiv\text{P}$, $0\text{ }^{\circ}\text{C}$, 1 h.

Kobayashi *et al.* demonstrated the formation of one of the first examples of a diphosphaabenzene upon refluxing 2,3,5,6,7,8-hexakis(trifluoromethyl)-7-methoxy-1,4-diphospha-bicyclo[2.2.2]octa-Z,5-diene in hexane, furnishing a fluorocarbon-substituted 1,4-diphoshabenene *via* an intramolecular rearrangement (Scheme 5).²⁰



Scheme 5: Synthesis of a diphoshabenzene. *Reagents and Conditions:* (i) RhCl_3 , MeOH , r.t.; (ii) hexane, reflux.

Understanding the electronic properties of phosphabenzene and its derivatives has been the focus of intensive study since their initial discovery. It is now well established that phosphinines are planar, aromatic molecules, but exhibit distinct properties compared to their carbon and nitrogen counterparts. Their coordination chemistry is of particular interest and quite different to that of the pyridine analogues, primarily due to the difference in their frontier molecular orbitals. While the nitrogen lone pair of C_5H_5N is associated with the HOMO, the lone pair of C_5H_5P is much lower in energy and associated with the HOMO-2. Additionally, the LUMO of pyridine is much higher in energy than that of phosphabenzene, the latter being heavily associated with the phosphorus centre. This renders phosphinines weak σ -donors, but strong π -acceptors, thereby facilitating η^1 -coordination to a metal centre.^{21–23} This is exemplified by the work of Ashe who reported the η^1 -phosphabenzene complex $[(C_3H_2Ph_3P)Mo(CO)_3]$ in 1976,²⁴ which was achieved *via* displacement of THF/CO from $[(THF) \cdot Mo(CO)_5]$ by 2,4,6-triphenylphosphabenzene. Nixon and co-workers later demonstrated the η^1 -coordination of the triphosphabenzene $C_3^tBu_3P_3$, reporting the complex $[(C_3^tBu_3P_3)PtCl_2(PMe_3)]$.²⁵ Interestingly, it was shown that the *s*-character of the phosphorus lone pair in this complex was reduced compared to that of the monophosphabenzene complex $[(C_3H_2^tBu_3P)PtCl_2(PMe_3)]$.

While the η^1 -bonding mode predominates, η^6 -coordination is also readily accessible (*vide supra*). Moreover, both η^1 - and η^6 -coordination can occur concurrently,^{26–28} with the first such examples reported by Nainan *et al.*, with preparation of the compounds $[(CO)_3M'(\eta^1:\eta^6-C_5H_4RP)M(CO)_5]$ (Figure 1). An analogous complex has since been synthesised by Nixon and co-workers of the form $[(CO)_3Mo(\eta^1:\eta^6-C_3^tBu_3P_3)PtCl_2(PEt_3)]$ with the previously reported triphosphabenzene ligand.^{29,30}

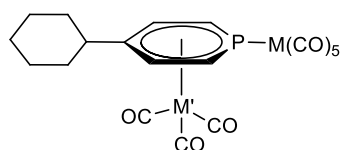


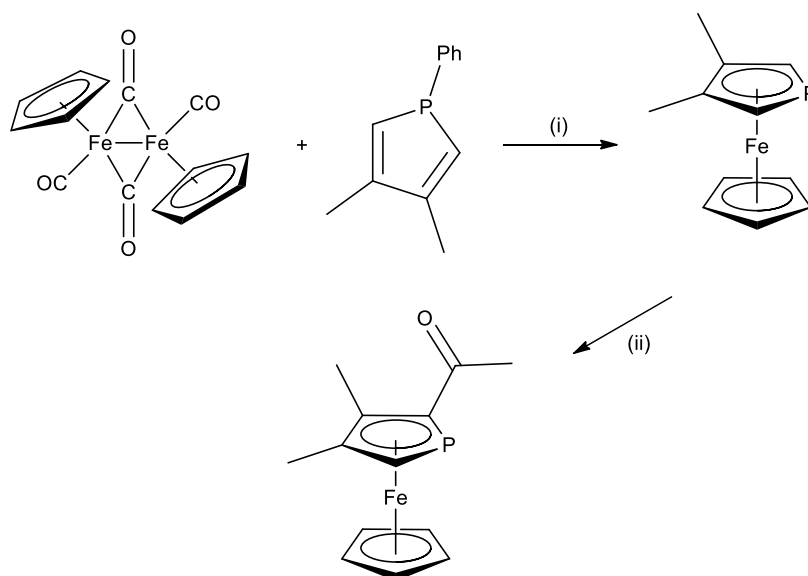
Figure 1: An $\eta^1:\eta^6$ -coordinated phosphabenzene ($M = M' = Cr$; $M = M' = Mo$; $M = Cr$, $M' = W$)

1.1.2 PHOSPHOLIDES

As the field of phosphinine chemistry was rapidly developing, attention also turned to the phospholides, analogues of the cyclopentadienyl ligand, with one or more CR units replaced with phosphorus. Similarly to phosphabenzenes, the phospholides have been found to exhibit a high level of aromaticity (>80%)^{31,32} and also undergo both η^1 -coordination and bonding

through the π -system in an η^5 - fashion.³³ The first complex of this type was published in 1971 by Braye *et al.*³⁴ The compounds $[\text{C}_4\text{H}_5\text{P}][\text{M}]$ (M = alkali metal) were prepared from the phosphole $\text{C}_4\text{H}_4\text{PPh}$, *via* cleavage of the P–Ph bond upon addition of an alkali metal. P–R cleavage – where R is often phenyl or a halogen – is one of the most common routes to access phospholides. However, alternative methods have since been established, with Becker demonstrating that phospholides can be obtained upon reaction of ${}^t\text{BuC}\equiv\text{P}$ with $\text{LiP}(\text{SiMe}_3)_2$, yielding the triphospholide anion $[\text{P}_3\text{C}_2{}^t\text{Bu}_2]^-$.³⁵ Nixon *et al.* later demonstrated similar reactivity with ${}^t\text{BuC}\equiv\text{P}$ upon addition of sodium amalgam, resulting in a mixture of the 1,3-di- and 1,3,4-triphospholide anions.³⁶ In more recent years, this chemistry has been extended to the silyl analogues, *i.e.* $[\text{P}_n\text{C}_{5-n}(\text{SiMe}_3)_{5-n}]^-$.^{37,38} Such compounds were furnished using the silyl-phosphaalkyne $\text{Me}_3\text{SiC}\equiv\text{P}$ *via* a number of preparative methods, such as refluxing with an alkali metal or reaction with a lithium reagent such as LiOMe , each time leading to a mixture of the 1,3-di- and 1,3,4-tri-phospholides. Additionally, it was observed that upon addition of the alkyl lithium reagents MeLi and ${}^n\text{BuLi}$, the 1,3-diphospholide ion $[\text{P}_2\text{C}_3(\text{SiMe}_3)_2]^-$ was furnished exclusively.

Phospholyl π -complexes of transition metals, specifically metallocene analogues, became particularly desirable targets given the extensive coordination chemistry demonstrated by the cyclopentadienyl ligand; much of the early work in this field focused on ferrocene derivatives. The first transition metal phospholyl complex was furnished *via* cleavage of the P–Ph bond of a phosphole upon its addition to the iron dimer $[\{\text{Cp}(\text{C}\equiv\text{O})(\text{Fe}-\text{C}=\text{O})\}_2]$ (Scheme 6).^{39,40} X-Ray diffraction data gave some insight into the structure of the resulting ferrocene derivative, with P–C bond lengths of 1.758(5)/1.768(5) Å and C–C bond lengths between 1.403(7) and 1.414(6) Å, somewhat longer than those observed for the C_5H_5^- ring (C–C = 1.378(12)–1.412(10) Å). Despite the phospholide ring deviating slightly from perfect planarity, with the phosphorus centre shifted 0.041(2) Å out of the plane, the aromaticity of these species was supported by the ability of the phospholide ring to undergo a classical Friedel–Crafts acylation.



Scheme 6: Friedel–Crafts acylation yielding a phospholide ligand. *Reagents and Conditions:* (i) xylene, 150 °C; (ii) CH_3COCl , AlCl_3 , DCM, 25 °C.

Nixon *et al.*⁴¹ later observed formation of complexes containing both η^5 -1,3-diphospholide and η^5 -1,3,4-triphospholide upon addition of $[\text{Li}(\text{dme})_3][\text{C}_2\text{R}_2\text{P}_3]$ to a solution of $[\text{FeCl}_2]$ in monoglyme. X-Ray diffraction data confirmed the structure of the 1,3-diphospholide ring, with P–C and C–C bond lengths similar to those of the unsubstituted phospholide ($d_{\text{PC}} = 1.798(7)$, $1.750(6)$ Å; $d_{\text{CC}} = 1.427(9)$ Å). Compounds of the type $\text{RC}\equiv\text{P}$ were later used in the pursuit of such complexes; a mixture of $^t\text{BuC}\equiv\text{P}$, $^i\text{PrC}\equiv\text{P}$ and Na in monoglyme was found to yield all nine variations of the di- and tri-phospholides, leading to a plethora of mixed ring sandwich complexes upon addition of $[\text{FeCl}_2]$.⁴² As for phosphinines, metal vapour synthesis has successfully yielded coordinated phospholides, with 1,3-di- and 1,3,4-tri-phospholide complexes of indium^{43,44} and the mixed sandwich complexes $[\text{Co}(\eta^5\text{-P}_3\text{C}_2^t\text{Bu}_2)(\eta^4\text{-P}_2\text{C}_2^t\text{Bu}_2)]$ and $[\text{Co}(\eta^5\text{-P}_2\text{C}_3^t\text{Bu}_3)(\eta^4\text{-P}_2\text{C}_2^t\text{Bu}_2)]$ successfully synthesised.⁴⁵

The first η^5 -1,2-diphospholide ligand, which also demonstrated η^1 -coordination of the phospholide ring through a phosphorus lone pair, was synthesised *via* a significantly different synthetic procedure.^{46–53} A mixture of $[(\text{C}_5\text{Me}_5)(\text{CO})_2\text{Fe}(\text{P}(\text{SiMe}_3)\text{–P}=\text{C}(\text{SiMe}_3)_2)]$ and $[\text{Cr}(\text{C}_8\text{H}_{14})(\text{CO})_5]$ in pentane furnished an η^1 -, η^5 -sandwich complex and the first 3-ferradiphosphaallyl complex (Figure 2).

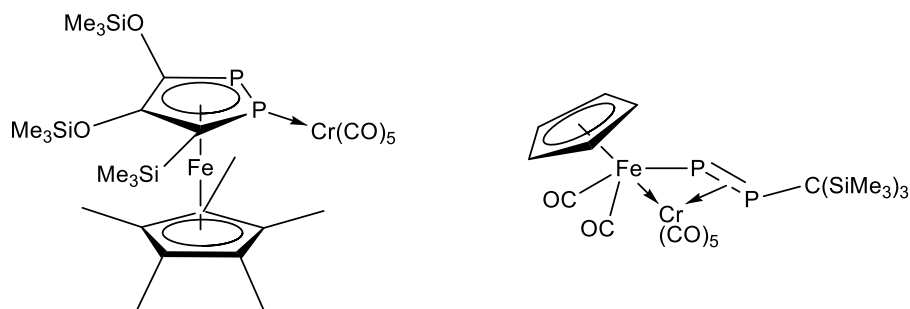
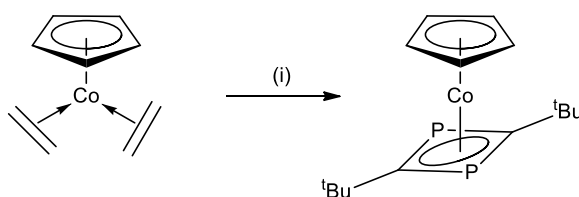


Figure 2: Products from the reaction of $[(C_5H_5)(CO)_5Fe(P(SiMe_3)-P=C(SiMe_3)_2)]$ and $[Cr(C_8H_{14})(CO)_5]$.⁴⁶

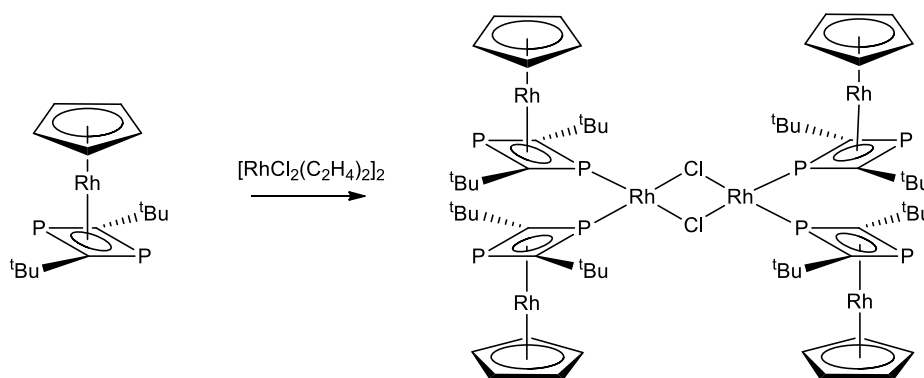
1.1.3 DIPHOSPHACYCLOBUTADIENES

In addition to the 6- and 5-membered aromatic heterocycles, diphosphacyclobutadienes have also been developed.^{54–60} The first diphosphacyclobutadiene complex was synthesised independently by both Binger⁶¹ and Nixon⁶² upon addition of two equivalents of $tBuC\equiv P$ to $[CpCo(C_2H_4)_2]$, resulting in a head-to-tail cyclodimerisation of the phosphalkyne units, yielding $[CpCo(P_2C_2tBu_2)]$ (Scheme 7). Nixon *et al.* were able to synthesise a number of analogues of the type $[Cp'M(P_2C_2tBu_2)]$ ($M = Rh$ or Ir and $Cp' = Cp$ or Cp^*), the identities of which were confirmed by X-ray diffraction studies of the compound $[Cp^*Co(P_2C_2tBu_2)]$. The P–C bonds lengths of the phosphabutadiene ring ranged from 1.79(1) Å to 1.82(1) Å, confirming a planar square conformation, akin to their carbon analogues; these bond lengths are substantially longer than that of the free phosphalkyne (1.54 Å) as might be expected.^{63,64}



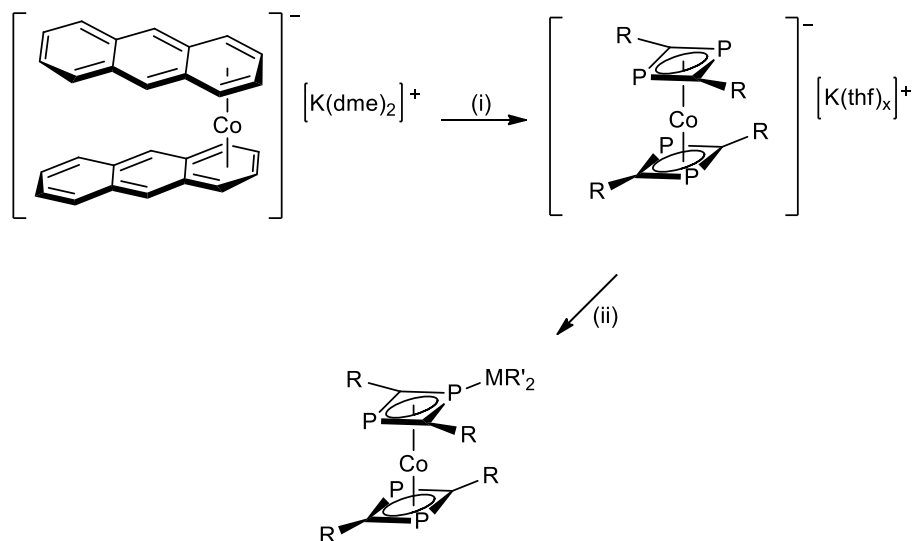
Scheme 7: Synthesis of the first coordinated 1,3-phosphabutadiene compound. *Reagents and Conditions:* (i) 2 $tBuC\equiv P$.

Diphosphacyclobutadienes are able to engage in both η^1 - and η^4 -coordination to metal centres, with a number of examples demonstrating both coordination modes within the same heterocycle. An early example of such a complex was demonstrated by Nixon and co-workers who were able to displace four equivalents of C_2H_4 from the rhodium dimer $[Rh_2Cl_2(C_2H_4)_4]$ by addition of an excess of $[CpRh(P_2C_2tBu_2)]$ (Scheme 8).^{65,66}



Scheme 8 Reaction of $[\text{CpRh}(\text{P}_2\text{C}_2^t\text{Bu}_2)]$ with $[\text{Rh}_2\text{Cl}_2(\text{C}_2\text{H}_4)_2]$.

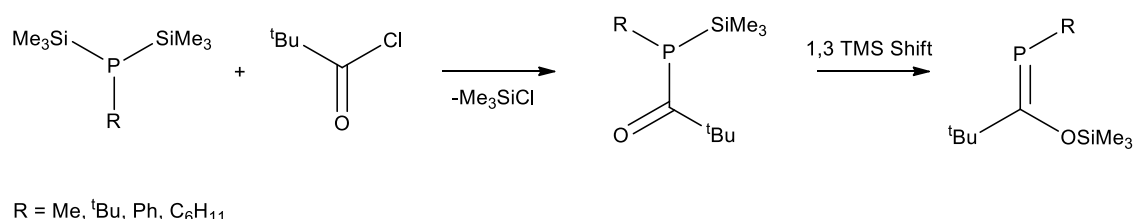
Recent work in this field has been reported by Wolf and co-workers with the synthesis of a series of diphosphacyclobutadiene cobaltate sandwich complexes, which further coordinate to a Au or Ag centre in an η^1 -fashion.^{67–69} These complexes were synthesised by addition of $\text{RC}\equiv\text{P}$ ($\text{R} = ^t\text{Pent}, \text{Ad}$) to the bis(anthracene)cobaltate complex $[\text{K}(\text{dme})_2\{\text{Co}(\eta^4\text{-C}_{14}\text{H}_{10})_2\}]$, furnishing the bis-(diphosphacyclobutadiene) complex shown in Scheme 9. Subsequent addition of $[\text{AuCl}(\text{PPh}_3)]$, AgCl or AgSbF_6 in the presence of PMe_3 led to the desired $\eta^1:\eta^4$ -complexes.



Scheme 9: Synthesis of $\eta^1:\eta^4$ -diphosphacyclobutadiene sandwich complexes. *Reagents and Conditions:* (i) 4 $\text{RC}\equiv\text{P}$, THF, 16 h, r.t.; (ii) $\text{AuCl}(\text{PPh}_3)$, AgCl or AgSbF_6 , PMe_3 , THF, 16 h, $-78\text{ }^\circ\text{C}$ ($\text{R} = \text{Ad}, ^t\text{Pent}$; $\text{R}' = \text{PMe}_3$; $\text{M} = \text{Au}, \text{Ag}$).

1.1.4 PHOSPHAALKENES AND PHOSPHAALKYNES

While the history of low-coordinate phosphorus began with the synthesis of aromatic heterocycles, much of the chemistry that has resulted from these seminal works, which has been discussed thus far has relied on access to phosphaaalkynes and phosphaaalkenes. It was in 1976 that Becker⁷⁰ synthesised the first stable, localized phosphorus–carbon multiple bond in the form of the phosphaaalkene $\text{RP}=\text{C}(\text{OSiMe}_3)(^t\text{Bu})$ ($\text{R} = \text{CH}_3, ^t\text{Bu}, \text{C}_6\text{H}_{11}, \text{Ph}$) upon spontaneous rearrangement of the keto-form $\text{R}(\text{Me}_3\text{Si})\text{P}-\text{C}(\text{O})(^t\text{Bu})$ *via* a 1,3-trimethylsilyl migration, driven by the oxophilicity of silicon (Scheme 10). Shortly thereafter the first stable phosphaaalkyne was synthesised, $^t\text{BuC}\equiv\text{P}$, again by Becker and co-workers,⁷¹ *via* elimination of hexamethyldisiloxane from $\text{Me}_3\text{SiP}=\text{C}(\text{OSiMe}_3)^t\text{Bu}$ upon addition of a base. A vast quantity of research has since stemmed from this pioneering work and has found application in areas such as organometallic synthesis and catalysis (*vide infra*).



Scheme 10: Becker's phosphaaalkene synthesis

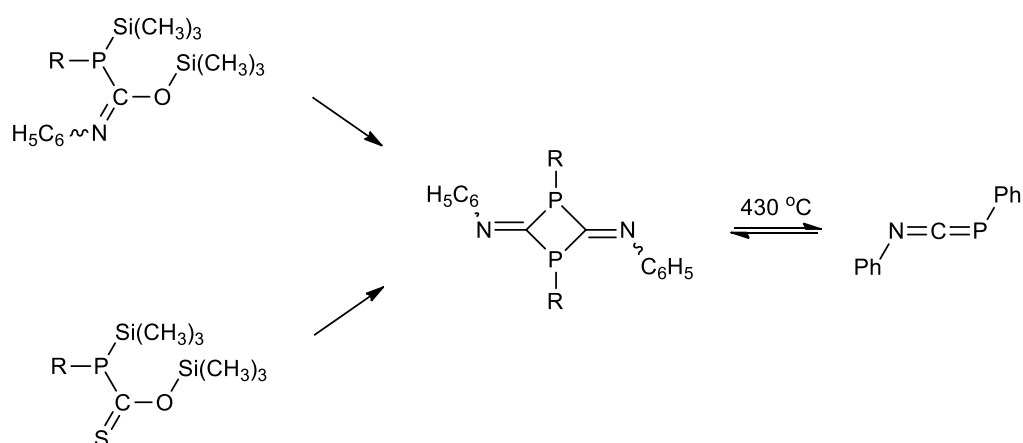
With a flurry of activity around the synthetic chemistry of the $\text{P}=\text{C}$ and $\text{P}\equiv\text{C}$ moieties in the 1960s and 1970s, experimental and theoretical studies began to shed some light on their structure and properties. Comparisons between the chemistry of $\text{C}=\text{C}$, $\text{C}=\text{P}$ and $\text{C}=\text{N}$ were made and demonstrated that the $\text{P}=\text{C}$ bond is more analogous to the $\text{C}=\text{C}$ than the $\text{C}=\text{N}$ bond. The electronegativity of phosphorus (2.2) is close to that of carbon (2.5), far more so than that of either nitrogen (3.0) or silicon (1.9); however, it is still slightly electropositive causing the $\text{P}=\text{C}$ bond to exhibit some polarity, though this polarity can be altered by varying the substituents.^{33,72} The $\text{C}=\text{P}$ systems stand apart from their $\text{C}=\text{N}$ counterparts due to the nature of their frontier molecular orbitals. The HOMO of $\text{H}_2\text{C}=\text{NH}$ is heavily associated with the nitrogen lone pair and is significantly higher in energy than the π -system (-10.62 eV and -12.49 eV, respectively);⁷³ consequently, $\text{C}=\text{N}$ reacts almost exclusively at the lone pair. In contrast to this, the HOMO of $\text{H}_2\text{C}=\text{PH}$ is associated with the π -system with a π -ionization energy of -10.30 eV and is much closer to that of ethene at -10.51 eV; the lone pair of $\text{H}_2\text{C}=\text{PH}$ lies at -10.70 eV.⁷³ The $\text{C}=\text{P}$ bond is therefore able to react at both sites and the ability of $\text{P}=\text{C}$ to mimic its carbon analogues is hindered predominantly by reactivity at the lone pair; however, this can often be circumvented by η^1 -coordination of the $\text{P}=\text{C}$ fragment to a metal centre through the phosphorus

lone pair. Additionally, the P=C bond has also been shown to act as a π -acceptor, with a LUMO resembling that of C=O.⁷⁴ As a result of these interesting properties, a great deal of attention has been paid to the organometallic and coordination chemistry of the P=C moiety.

In contrast, the phosphorus lone pair of the C \equiv P moiety lies at a significantly lower energy than that of the π -system (−11.44 eV and −9.61 eV, respectively), further demonstrating the similarity between C–P and C–C multiple bonds ($\pi_{C\equiv C} = -11.40$ eV).⁷⁵ Consequently, reactivity at the π -system is more commonly observed, which potentially allows for more alkyne-like chemistry to occur. While polarity of the C \equiv P bond (which bears a δ^+ phosphorus) is more exaggerated than that of the C=P bond, it too can be modified by varying the substituents about the carbon and phosphorus centres.⁷⁶

1.1.5 PHOSPHACUMULENES

The first phosphacumulenes – compounds of the type R=P=C=R' – were reported by Kolodiaznyy. The compound ^tBuP=C=N^tBu was furnished *via* the Becker synthesis, with elimination of hexamethyldisiloxane from ^tBu(Me₃Si)P–C(OSiMe₃)=(N^tBu).⁷⁷ Despite this seminal work, Wentrup *et al.* demonstrated that the synthesis of phosphacumulenes is not facile, with their attempts to synthesise the analogous complexes RP=C=N(C₆H₅) leading to a [2+2] cycloaddition, furnishing a 4-membered heterocycle.⁷⁸ It was found that flash vacuum pyrolysis of the dimeric product could generate the desired phosphacumulene RP=C=N(C₆H₅), however, at temperatures above −55 °C, the cycloadduct was reformed (Scheme 11).



Scheme 11: Formation of an unstable phosphacumulene (R = Ph, ^tBu, C₂H₅, Mes).

Shortly thereafter, Yoshifuji *et al.* reported the synthesis of the first 1-phosphaallene and

diphosphaallene.^{79,80} The 1-phosphaallene, $\text{Mes}^*\text{P}=\text{C}=\text{CPh}_2$, was furnished upon addition of $\text{Ph}_2\text{C}=\text{C}=\text{O}$ to the lithiated phosphide $\text{Mes}^*\text{P}(\text{Li})\text{SiMe}_2^t\text{Bu}$ with subsequent loss of the lithiated siloxide $^t\text{BuMe}_2\text{SiO}^-$. The diphosphaallene was synthesised in similar fashion, with addition of CO_2 to the lithiated phosphide $\text{Mes}^*\text{P}(\text{Li})\text{SiMe}_2^t\text{Bu}$, furnishing the phosphalkene–phosphine compound $\text{Mes}^*\text{P}=\text{C}(\text{OSiMe}_2^t\text{Bu})\text{P}(\text{H})\text{Mes}^*$. Subsequent addition of BuLi gave rise to the diphosphaallene $\text{Mes}^*\text{P}=\text{C}=\text{PMes}^*$ in good yield.

Yoshifuji and co-workers were also able to obtain the first phosphaallene coordination complex by addition of the diphosphaallene $\text{ArP}=\text{C}=\text{PAr}$ to $[\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]$, yielding $[(\text{Ph}_3\text{P})_2\text{Pt}(\text{ArP}=\text{C}=\text{PAr})]$ with η^2 -coordination of one $\text{P}=\text{C}$ bond to the Pt centre (Figure 3).⁸¹

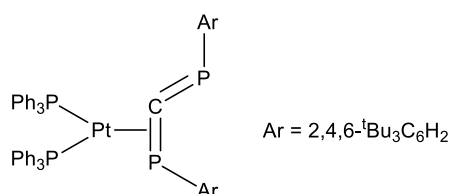


Figure 3: The first diphosphaallene coordination compound⁸¹

1.2 PHOSPHAALKENES

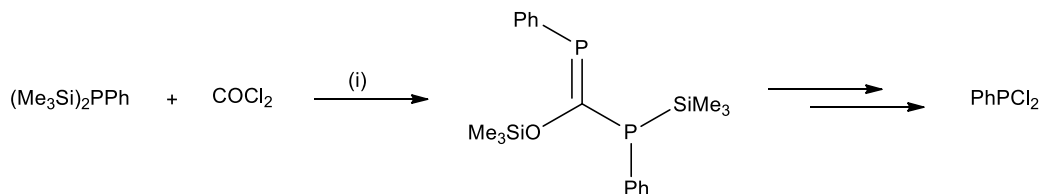
1.2.1 SYNTHESIS AND PROPERTIES OF ORGANO-PHOSPHAALKENES

Since Becker's pioneering work on acyclic phospho-organic compounds with the formation of $\text{RP}=\text{C}(\text{OSiMe}_3)(^t\text{Bu})$, numerous methods of organo-phosphaalkene preparation have emerged, which are often based on classical alkene synthesis.⁷⁶ Such synthetic routes include variations of the aforementioned 1,3-silatropic migration (Scheme 10), 1,2-elimination reactions, adaptations of the Peterson olefination and Wittig reactions, and double bond migration.^{82–84}

1.2.1.1 1,3-silatropic migration

Becker's method of phosphaalkene formation *via* 1,3-silatropic migration has been implemented extensively in the pursuit of low-coordinate phosphorus compounds.^{85–88} However, prior to the publication of this work, Langer *et al.* had synthesised $(\text{P}(\text{C}_6\text{H}_5)_2)_2\text{CO}$ upon addition of phosgene to $\text{PhP}(\text{SiMe}_3)_2$ at $-110\text{ }^\circ\text{C}$. They noted that at $-60\text{ }^\circ\text{C}$ or higher, evolution of CO occurred and the reaction was unsuccessful.⁸⁹ It was not until after the publication of Becker's seminal work that Appel *et al.* were able to show that upon repeating Langer's 'failed' reaction, a number of intermediates can be isolated, including the phosphaalkene

$\text{PhP}=\text{C}(\text{OSiMe}_3)\text{PPh}(\text{SiMe}_3)$, which reacts further with COCl_2 to produce PhPCl_2 with loss of CO (Scheme 12).⁹⁰ This phosphalkene–phosphine was characterised by two mutually coupled doublets in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at δ_{P} 164 and -37 ($^2J_{\text{PP}} = 72.8$ Hz), assigned to the $\text{P}=\text{C}$ and $\text{P}-\text{Si}$ phosphorus centres, respectively. Additionally, a multiplet at δ_{C} 205.3 (dd, $^1J_{\text{CP}} = 78.9$, 37.7 Hz) in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum was assigned to the phosphalkenic carbon centre. Appel later extended this work to synthesise the first phosphaketene upon addition of phosgene to $^t\text{BuPR}(\text{SiMe}_3)$ ($\text{R} = \text{H}, \text{SiMe}_3$), furnishing $^t\text{BuP}=\text{C}=\text{O}$.⁹¹



Scheme 12: 1,3-silotropic migration leading to a phosphalkene–phosphine. *Reagents and Conditions:* (i) pentane, 6 h, 0 °C.

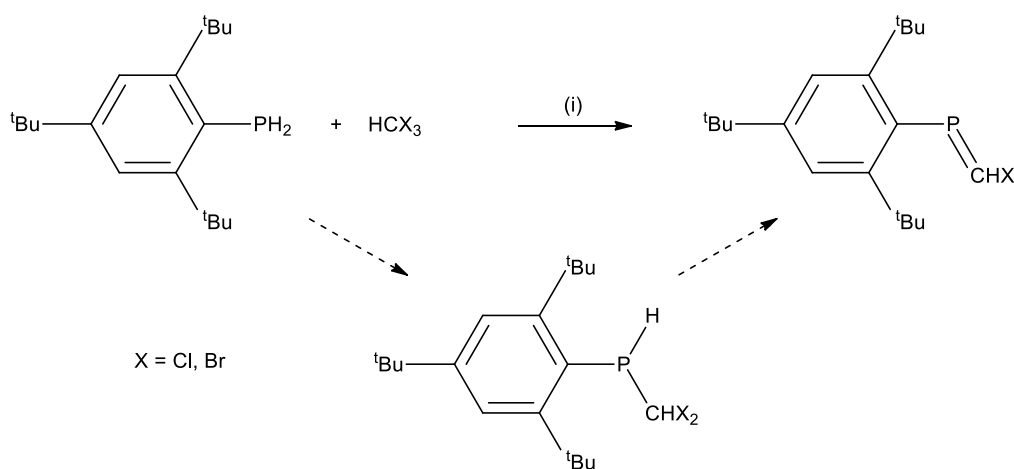
Appel and co-workers were also the first to demonstrate that phosphalkenes formed *via* a 1,3-silotropic rearrangement can be accessed through an imide rather than a carbonyl functionality.^{92,93} Condensation of $\text{PhP}(\text{SiMe}_3)_2$ with $\text{Cl}_2\text{C}=\text{NPh}$ in a 2:1 ratio yields the phosphalkene–phosphine $\text{PhP}=\text{C}(\text{NPh}(\text{SiMe}_3))(\text{PPh}(\text{SiMe}_3))$, with the proposed intermediate $\text{Ph}(\text{Me}_3\text{Si})_2\text{P}-\text{C}(\text{Cl})=\text{NPh}$ having undergone a 1,3-silotropic shift to yield $\text{PhP}=\text{C}(\text{NPh}(\text{SiMe}_3))$. Schmidt and co-workers later extended this work, demonstrating that a range of other imides other than phosgene analogues were feasible starting materials for such transformations, including carbodiimides ($\text{R}'\text{N}=\text{C}=\text{NR}''$) and acyl chloride derivatives ($\text{ClR}'\text{C}=\text{NR}''$).^{94,95}

1.2.1.2 Condensation/1,2-elimination reactions

Synthesis of phosphalkenes has also been demonstrated through an initial condensation reaction followed by a 1,2-elimination step, a notable example being that of Bickelhaupt's aryl-phosphalkene, $\text{ArP}=\text{C}(\text{C}_6\text{H}_5)_2$. This compound was formed *via* an initial condensation reaction upon addition of $\text{LiCH}(\text{C}_6\text{H}_5)_2$ to RPhCl_2 , followed by dehydrohalogenation of $\text{ArP}(\text{C}_6\text{H}_5)_2\text{CH}(\text{C}_6\text{H}_5)_2$ upon addition of DBU. This was the first example of an all carbon substituted phosphalkene and was characterised by ^{31}P NMR spectroscopy; a $\text{P}=\text{C}$ phosphorus resonance at δ_{P} 233.1 was considered consistent with an sp^2 -hybridized phosphorus centre, being similar to those reported by Becker and Appel.⁹⁶

Meyer and co-workers⁹⁷ also implemented this synthetic approach successfully, with the

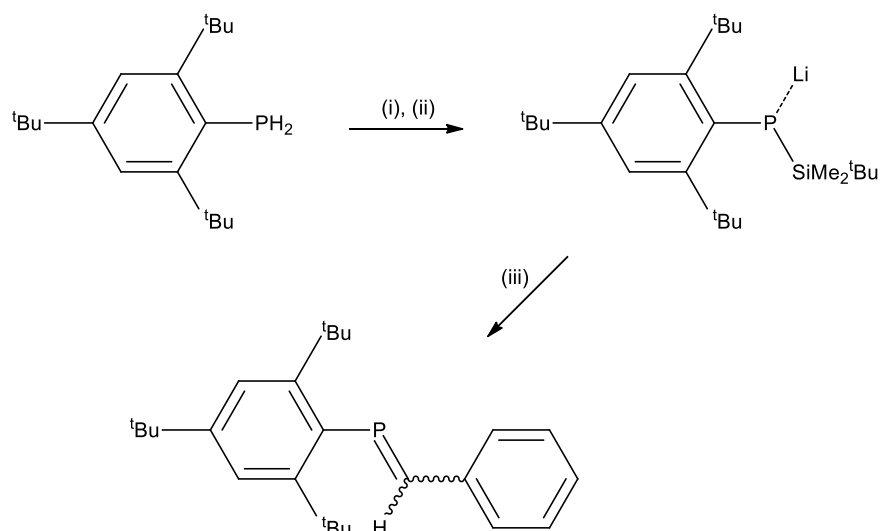
formation of $\text{ArP}=\text{CR}(\text{NMe}_2)$ ($\text{Ar} = \text{Ph}, \text{Mes}$; $\text{R} = \text{H}, \text{CH}_3$) upon heating a mixture of ArPH_2 and $\text{CR}(\text{OMe})_2(\text{NMe}_2)$ for 1 h, with subsequent loss of MeOH . Similarly, Appel *et al.*,⁹⁸ were able to synthesise $\text{Mes}^*\text{P}=\text{CHX}$ ($\text{X} = \text{Cl}, \text{Br}$) by reacting the primary phosphine Mes^*PH_2 with HCX_3 , resulting in loss of 2 equivalents of HX ; the $\text{Mes}^*\text{HP}-\text{CX}_2\text{H}$ intermediate was observed spectroscopically, with phosphorus resonances at $\delta_{\text{P}} -24.6$ and -16.9 when $\text{X} = \text{Cl}$ and Br , respectively (Scheme 13). Phosphorus resonances of the resultant phosphalkenes were observed at $\delta_{\text{P}} 250.2$ (Cl) and 262.4 (Br), again consistent with formation of a $\text{P}=\text{C}$ bond. Formation of such compounds was only achievable with sterically bulky aromatic groups attached to phosphorus.



Scheme 13: Synthesis of a $\text{Mes}^*\text{P}=\text{CHX}$ via double dehydrohalogenation. *Reagents and Conditions:* (i) KOH , THF , 24 h.

1.2.1.3 Phospha-Peterson Reaction

The carbon–phosphorus analogy is particularly well illustrated by an adaptation of the Peterson olefination, with some of the pioneering work in this field led by Yoshifuji and Geoffroy.^{99,100} As illustrated in Scheme 14, deprotonation of the phosphine with $^n\text{BuLi}$ and addition of $\text{ClSiMe}_2^t\text{Bu}$ followed by benzaldehyde results in loss of siloxide to yield a $\text{P}=\text{C}$ bond. The resultant product, which is obtained as the *E*-isomer, can be isomerised to the *Z* isomer by UV irradiation; the latter isomer exhibits a notably higher-field ^{31}P chemical shift (*E*- = $\delta_{\text{P}} 259.3$ ($^2J_{\text{PH}} = 26.9$ Hz); *Z*- = $\delta_{\text{P}} 241.6$ ($^2J_{\text{PH}} = 39.1$ Hz)). It has since been established that *E*- and *Z*-phosphalkene isomers can be differentiated by a trend toward enhanced shielding of the $\text{P}=\text{C}$ phosphorus centre of the *Z*-isomer; in this case, the vinylic protons and $\text{P}=\text{C}$ carbon centres mirror this shielding effect (*E*- = $\delta_{\text{H}} 8.12$ (CH), $\delta_{\text{C}} 175.8$ ($\text{P}=\text{C}$); *Z*- = $\delta_{\text{H}} 7.80$ (CH), $\delta_{\text{C}} 162.7$ ($\text{P}=\text{C}$)).¹⁰¹ Additionally, larger J_{PH} spin–spin couplings are generally observed for *Z*-isomers.¹⁰²

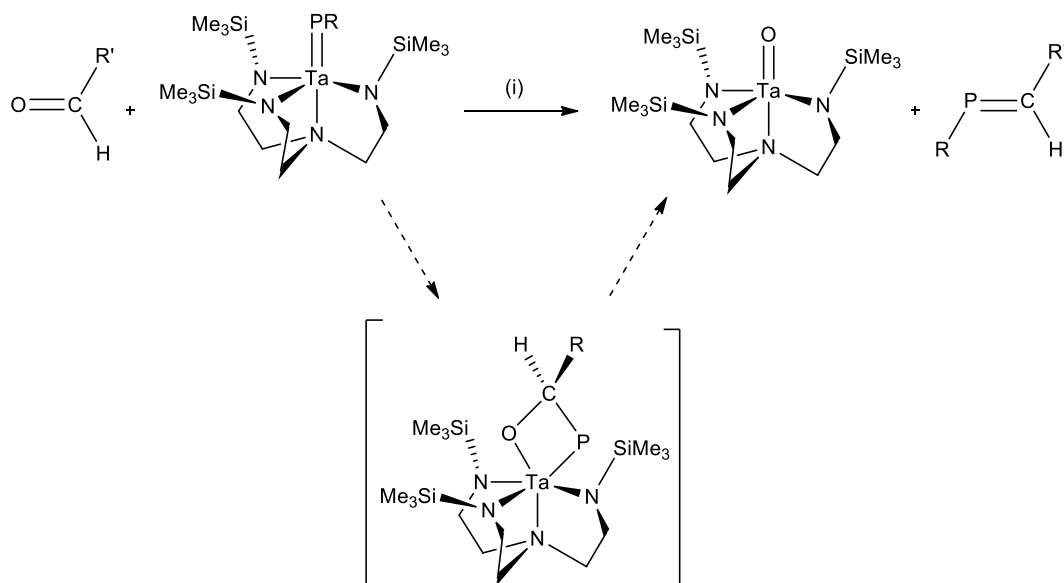


Scheme 14: Synthesis of a phosphalkene *via* an adapted Peterson Olefination reaction.

Reagents and Conditions: (i) $n\text{BuLi}$, THF; (ii) $\text{ClSiMe}_2^t\text{Bu}$; (iii) PhCHO .

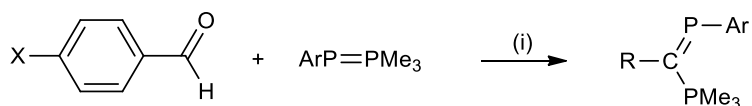
1.2.1.4 Phospha-Wittig Reaction

Another common method of alkene synthesis is the Wittig reaction, which has also been adapted in the pursuit of $\text{P}=\text{C}$ bonds. In 1993, Schrock and co-workers developed the tantalum phosphinidene complex $(\text{N}_3\text{N})\text{Ta}=\text{PR}$ (where $\text{N}_3\text{N} = (\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}$; $\text{R} = \text{Ph}, \text{Cy}, ^t\text{Bu}$).^{103,104} Reactions of these compounds with bulky aromatic aldehydes led to formation of phosphalkenes as shown in Scheme 15. Formation of the phosphalkene is believed to arise from $\text{C}=\text{O}$ addition across the $\text{Ta}=\text{P}$ bond, forming a 4-membered metallacyclic intermediate. Similar phosphinidenes have since been utilised in the pursuit of phosphalkenes.^{105–107}



Scheme 15: Phosphaalkene synthesis *via* a tantalum phosphinidene. An adaptation of the Wittig reaction. *Reagents and Conditions:* (i) DCM, 7 h, 95 °C.

Alternative phospha-Wittig reagents have since been developed, with a noteworthy example illustrated by Protasiewicz *et al.*,^{108,109} who demonstrated for the first time the phospha-Wittig reaction without the assistance of a transition-metal based fragment. Addition of the phosphanylidene- σ^4 -phosphorane complexes $\text{ArP}=\text{PMe}_3$ ($\text{Ar} = \text{dmp}$, Mes^*) to aldehydes of the type $(p\text{-C}_6\text{H}_4\text{X})\text{CHO}$ ($\text{X} = \text{H}, \text{Cl}, \text{NO}_2, \text{OMe}, \text{NMe}_2$) resulted in formation of the phosphaalkenes $(p\text{-C}_6\text{H}_4\text{X})\text{CH}=\text{PAr}$ (Scheme 16). Despite Protasiewicz's phospha-Wittig reagent being a direct analogue of the traditional phospha-ylid reagent, it suffers from the same drawback as Schrock's phosphinidenes, in that the stability of the resultant phosphaalkenes relies heavily on bulky aromatic groups. In addition, the reaction is aldehyde-specific and cannot be extended to ketones or other carboxyl functional groups. Prior to this innovative work, the phospha-Wittig reaction had already been developed to synthesise metalla-phosphaalkenes (discussed in Section 1.2.2).⁷⁶



Scheme 16: 'Phospha-Wittig' reaction to form phosphaalkenes ($\text{X} = \text{H}, \text{Cl}, \text{NO}_2, \text{OMe}, \text{NMe}_2$; $\text{Ar} = \text{dmp}, \text{Mes}^*$). *Reagents and Conditions:* (i) THF.

1.2.1.5 1,3-sigmatropic rearrangements

Synthesis of the P=C moiety *via* double bond migration through a 1,3-sigmatropic rearrangement was discovered fortuitously by Mathey and co-workers in 1989.¹¹⁰ The unexpected, thermally induced 1,3-hydrogen migration within a secondary vinylphosphine resulted in the phosphalkene $\text{Mes}^*\text{P}=\text{CMe}_2$. While this complex was found to be stable due to the steric bulk of the Mes^* group, the product was formed in admixture with the parent vinylphosphine, with the two products found to be inseparable. Gates and co-workers have since demonstrated that base-induced 1,3-hydrogen migration is a viable route to phosphalkenes, with the addition of DBU or DABCO to secondary vinylphosphines of the type $(\text{C}_6\text{H}_2\text{CF}_3\text{R})\text{PHC(R')CH}_2$ furnishing the corresponding phosphalkenes $(\text{C}_6\text{H}_2\text{CF}_3\text{R})\text{P}=\text{CR'CH}_3$.^{111,112} However, Gates' example required very sterically bulky and electron-withdrawing substituents in order to exclusively form the phosphalkene, thereby limiting the application of this synthetic method.

1.2.2 COORDINATION CHEMISTRY OF PHOSPHAALKENES

The coordination chemistry of phosphalkenes provides an opportunity to finely tune the electronic properties of the P=C bond and have greater control over the degree of steric bulk surrounding it. Five coordination modes of phosphalkenes have been established theoretically (Figure 4). While all five types have been synthesised, it has become apparent that η^1 -coordination through the phosphorus lone pair (Figure 4, type **A**) and η^2 -coordination through the π -system (Figure 4, type **B**) are the most readily accessible of the bonding modes.¹¹³ While there are also a number of compounds of type **D** known, literature reports of compounds of type **C** and **E** remain scarce.

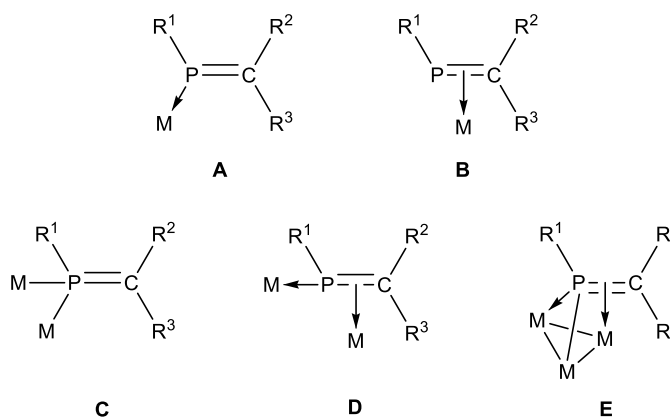
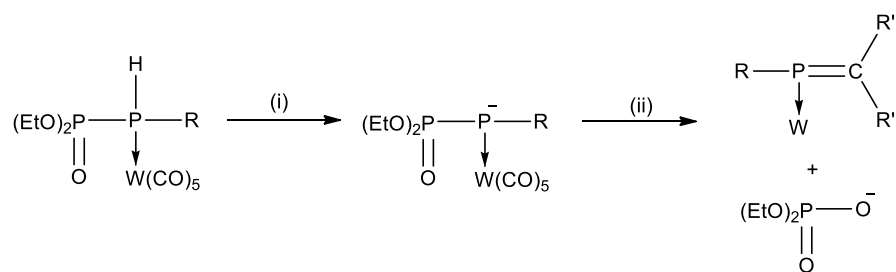


Figure 4: The Five Bonding Modes of Coordinated Phosphalkenes

The first examples of compounds of type **A** were synthesised by Kroto and Nixon¹¹⁴ and by Bickelhaupt¹¹⁵ in quick succession. Bickelhaupt's chromium complex $[(\text{CO})_5\text{Cr}(\text{P}(\text{Mes})=\text{C}(\text{C}_6\text{H}_5)_2)]$ was synthesised by reaction of $[\text{Cr}(\text{CO})_5\cdot(\text{THF})]$ with the parent phosphalkene, $(\text{Mes})\text{P}=\text{CPh}_2$, in THF under ambient conditions in an 89% yield. Notably, the parent phosphalkene and coordinated phosphalkene show little difference in the relative frequency of their phosphorus resonances in a ^{31}P NMR spectrum (δ_{P} 233.06 and 237.3, respectively). These data combined with a P=C bond length of 1.679 Å, which is similar to that of free phosphalkenes, demonstrate that, electronically, there is little effect on the phosphalkene upon η^1 -coordination in this instance. Kroto and Nixon were able to synthesise a number of different **A**-type complexes, using $(\text{Mes})\text{P}=\text{CPh}_2$. The complexes $[\text{cis-M}(\text{CO})_4(\text{P}(\text{Mes})=\text{CPh}_2)_2]$ (M = Cr, Mo, W) exhibited phosphorus resonances of δ_{P} 237, 223 and 195, respectively, again showing little difference in the phosphorus resonance upon coordination. A greater degree of shielding upon moving down the group 6 elements is to be expected due to the greater electron density on the metal centre. The bonding mode within the tungsten was further supported by tungsten satellites observed in the ^{31}P NMR spectrum ($^1J_{\text{WP}} = 264$ Hz).

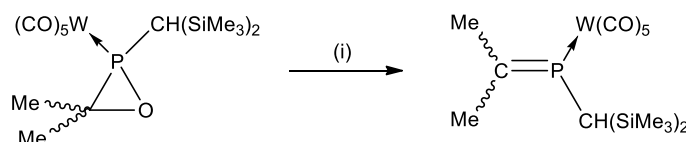
Phospha-Wittig reactions offer an alternative route to type **A** phosphalkenes. This novel approach to phosphalkene formation was initially demonstrated by Mathey and co-workers, who were able to synthesise the η^1 -phosphalkenes $[(\text{CO})_5\text{W} \leftarrow \text{P}(\text{R})=\text{CHR}']$ via phosphorylphosphine complexes of the type $[(\text{CO})_5\text{W}(\text{RP}(\text{H})-\text{P}(\text{O})(\text{OEt})_2)]$ (Scheme 17).¹¹⁶ X-Ray diffraction data for the Z-isomer of the complex $[(\text{CO})_5\text{W} \leftarrow \text{P}(\text{Ph})=\text{CH}(\text{CHMe}_2)]$ revealed a P=C bond length consistent with other reported η^1 -bound phosphalkenes ($d_{\text{C}=\text{P}}$ 1.64(1) Å), while phosphorus NMR resonances at δ_{P} 184 and 189 ($^1J_{\text{WP}} = 258.8$) were assigned to the E- and Z- isomers, respectively. It was again noted that steric bulk was necessary to stabilise the resultant phosphalkene.¹¹⁷



Scheme 17: Phospha-Wittig reaction yielding an η^1 -coordinated phosphalkene (R = Ph, Me; R'.

Reagents and Conditions: (i) $^n\text{BuLi}$, THF, -70°C ; (ii) $\text{R}'_2\text{C}=\text{O}$, DBO, $\text{C}_6\text{H}_6\text{:C}_5\text{H}_{12}$ (1:2).

More recently, Streubel and co-workers offered a new methodology for the synthesis of η^1 -phosphaalkenes by activating a 3-membered oxaphosphirane ring with CpTiCl_3 , ultimately yielding a phosphaalkene η^1 -coordinated to tungsten (Scheme 18); this represents another interesting example of an extrapolation of methodology for C=C bond formation.^{118,119} Bond lengths consistent with an η^1 -P=C bond were observed, while $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy demonstrated formation of both *E*- and *Z*- isomers ($d_{\text{C=P}}$: 1.669(5) Å; δ_{P} 181.1 ($^1J_{\text{WP}} = 253.7$); 172.3 ($^1J_{\text{WP}} = 254.5$)).



Scheme 18: Synthesis of an η^1 -coordinated phosphaalkene *via* an oxaphosphirane. *Reagents and Conditions:* (i) $[\text{TiCpCl}_3]/\text{Zn}$, THF, 16 h, r.t.

The η^1 -bonding mode of phosphaalkenes has been exploited to design novel ‘pincer’ ligands – bidentate ligands that coordinate to a metal centre *via* two donors. Such ligands have been prepared through many of the synthetic approaches previously discussed. One of the first examples was developed by Geoffroy and co-workers,¹⁰⁰ who synthesised the first polydentate complex incorporating two phosphaalkenyl units and a pyridine spacer $(\text{C}_5\text{H}_3\text{N})(\text{C}(\text{H})=\text{P}(\text{C}_6\text{H}_2^t\text{Bu}_3))_2$; the phosphaalkene fragments were accessed *via* the phospho-Peterson olefination (*vide supra*). This work has since led to a plethora of analogous complexes, with recent examples reported by Ozawa and co-workers who have synthesised group 8 complexes incorporating modified versions of Geoffroy’s bis(phosphaalkene).^{120,121} Not only are these compounds able to act as polydentate ligands, the planarity of the phosphaalkenyl units with respect to the pyridine ring can allow for conjugation across the ligand and lengthening of the P=C bonds; additionally, the extent of conjugation can be controlled by varying the substituents on the P=C fragment.

Ozawa and co-workers have also demonstrated the unique properties of pincer ligands incorporating the P=C moiety.¹²² Upon reaction of 2,6-bis(1-phenyl-2-phosphaethenyl)pyridine (BPEP) with FeBr_2 in the presence of KC_8 , the low-valent Fe^{I} complex, $[\text{FeBr}(\text{BPEP})]$, is formed (Figure 5). Stabilisation of the Fe^{I} centre arises due to the ability of the two low-lying π^* orbitals of the P=C bonds to interact with the d_z^2 orbital of Fe; a 15-electron Fe^{I} centre was thus achieved.

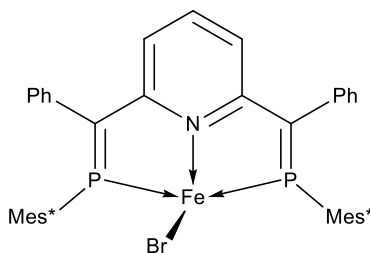


Figure 5: FeBr(BPEP)

Phosphaalkene complexes of type **B** were first exemplified with the synthesis of $[(\text{Me}_3\text{P})_2\text{Ni}((\text{Me}_3\text{Si})_2\text{C}(\eta^2\text{-P}=\text{C})\text{H}(\text{SiMe}_3)_2)]$ by reaction of $[(\text{Me}_3\text{P})_2\text{NiCl}_2]$ with $((\text{SiMe}_3)_2\text{CH})_2\text{PNa}$.¹²³ The novel nickel complex was characterised by data from X-ray diffraction studies and exhibited a $\text{P}=\text{C}$ bond length of 1.773(8) Å; this lies approximately half way between a $\text{P}-\text{C}$ single bond (*ca.* 1.85 Å) and a $\text{P}=\text{C}$ double bond (*ca.* 1.67 Å) as observed for free phosphaalkenes.¹⁰² This bond length was deemed consistent with η^2 -coordination, as back-donation from filled metal d-orbitals into the low-lying π^* -orbitals of the $\text{P}=\text{C}$ bond causes lengthening of the bond.¹²⁴ In addition, ^{31}P NMR spectroscopic analysis of the crude product revealed phosphorus resonances between δ_{P} 23 and -19 ; these data are markedly different from those of their η^1 -ligated counterparts. Angelici and co-workers similarly observed this upfield shift in the $\text{P}=\text{C}$ phosphorus resonance with the complexes $[(\text{R}_3\text{P})_2\text{Pd}(\eta^2\text{-C}(\text{Cl})_2=\text{PN}(\text{SiMe}_3)_2)]$ ($\text{R} = \text{Et}, \text{Ph}$) ($\delta_{\text{P}} = 38.0$ (Et); 41.8 (Ph)).^{125,126}

Extending the work of Cowley *et al.*, Bickelhaupt and co-workers demonstrated that the nature of the ancillary ligands around the metal centre had a significant impact on whether η^1 - or η^2 -coordination predominated.¹²⁷ Data obtained for the complex $[(\text{CO})_3\text{Ni}(\eta^1\text{-C}(\text{Ph})_2=\text{P}(\text{Mes}))]$ were typical of those seen in η^1 -coordinated complexes, with a $\text{P}=\text{C}$ phosphorus resonance observed at δ_{P} 211.3. However, the analogous complex $[(\text{bipy})\text{Ni}(\eta^2\text{-C}(\text{Ph})_2=\text{PXyl})]$ (Xyl = 2,6-dimethylphenyl) exhibited features characteristic of η^2 -coordination, exemplified by a $\text{P}=\text{C}$ phosphorus resonance of δ_{P} -16.1 . Notably, the $\text{P}-\text{C}$ bond length was longer than that generally observed for an η^2 -bound $\text{P}=\text{C}$ fragment ($d_{\text{P}=\text{C}} = 1.832(6)$ Å) and close to that expected of a $\text{P}-\text{C}$ single bond due to strong π -back donation.

A particularly interesting example of the transition between the η^1 - and η^2 -bonding modes demonstrated that both could exist within the same molecule in equilibrium.^{128,129} It was found that while in solution the complex $[(\text{Ph}_3\text{P})_2\text{Pt}(\text{C}(\text{Ph})_2\text{P}(\text{Mes}))]$ favoured η^2 -coordination; however, in the solid state η^1 -coordination was observed exclusively, as evidenced by X-ray diffraction data and solid-state ^{31}P NMR spectroscopy. Such observations were further

supported by van Koten and co-workers,¹³⁰ who demonstrated that by changing the ancillary ligands to yield the complex $[(\text{Cy}_3\text{P})_2\text{Pt}(\text{C}(\text{Ph})_2\text{P}(\text{Mes}))]$, η^1 -coordination was observed exclusively. However, with bulkier substituents on the $\text{P}=\text{C}$ carbon, η^2 -coordination was observed exclusively (Figure 6).

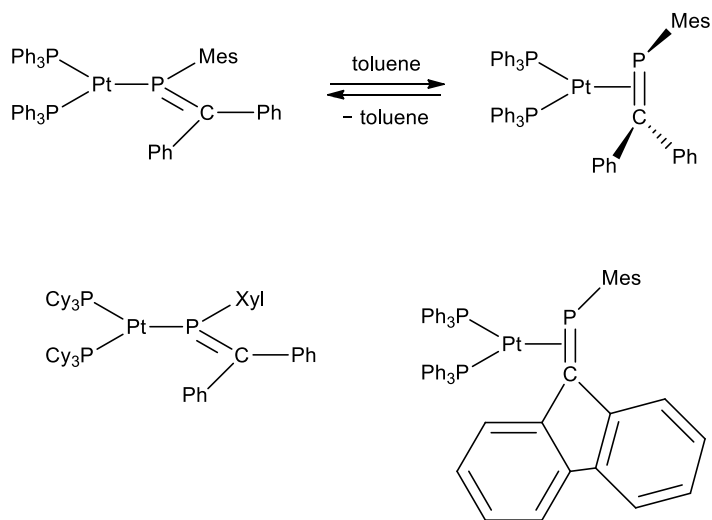


Figure 6: η^1 - and η^2 -coordination of phosphalkenes in Pt complexes, with a range of substituents dictating the bonding mode.^{128,130}

Compounds of type **D** are also accessible, with a phosphalkene η^1 -coordinated to a metal centre in conjunction with η^2 -coordination to a second metal centre.^{131–133} The first example of such a complex was demonstrated by Mathey and co-workers,¹³⁴ with the synthesis of $[(\text{C}_4\text{H}_2\text{Me}_2\text{P})\text{W}_2(\text{CO})_{10}]$ upon addition of $\text{C}_4\text{H}_2\text{MePLi}$ to $[\text{W}(\text{CO})_5(\text{THF})]$ in the presence of AlPh_3 , and subsequent protonation. The complex was characterized by X-ray diffraction and ^{31}P NMR data, which are consistent with an η^2 -coordinated $\text{P}=\text{C}$ bond ($d_{\text{P}=\text{C}} = 1.78(1) \text{ \AA}$; $\delta_{\text{P}} -31.9$).

More recently, Mays *et al.* synthesised the di-molybdenum complex $[\text{Cp}_2(\text{OC})_4\text{Mo}_2(\mu-\eta^1:\eta^2-\text{P}(\text{Ph})=\text{C}(\text{H})\text{Me})]$, which exhibited a $\text{P}=\text{C}$ bond length of $1.754(7) \text{ \AA}$ and $\text{Mo}-\text{P}$ bond lengths similar to those of Mathey's complex, with the longer bond corresponding to the $\eta^2-\text{C}=\text{P}-\text{Mo}$ fragment ($d_{\text{MoP}} = 2.435(2), 2.346(2) \text{ \AA}$).¹³⁵ Double protonation of this species led to loss of an alkylphosphine and formation of the oxygen bridge di-molybdenum complex $[\text{Cp}_2(\text{CO})_8\text{Mo}_2(\text{O})][\text{BF}_4]_4$.¹³⁶

The fine balance in alternating between the different bonding types, **A**, **B** and **D**, was demonstrated by Appel *et al.*, who synthesised the di-iron complex $[(\text{CH}_2=(\text{Mes}^*)\text{P})\text{Fe}_2(\text{CO})_8]$ upon addition of $\text{Mes}^*\text{P}=\text{CH}_2$ to 2 equivalents of $\text{Fe}_2(\text{CO})_9$, which exhibits both η^1 - and η^2 -

coordination within the same compound in a bimetallic complex. However, addition of only 1 equivalent of $\text{Fe}_2(\text{CO})_9$ led to a mixture of two compounds with one exhibiting η^1 -coordination and the other η^2 -, with both complexes of the formula $[(\text{CH}_2=(\text{Mes}^*)\text{P})\text{Fe}(\text{CO})_4]$.¹³⁷

1.2.3 METALLAPHOSPHAALKENES

The first example of a metallaphosphaalkene was published in 1985 by Weber and co-workers,¹³⁸ who had surmised that in addition to the established coordination chemistry of phosphaaalkenes, it should also be possible to replace one or more of the R groups with a metal fragment; this leads to five possible structures for the proposed metallaphosphaalkenes (Figure 7). Compound types **I** and **II**, usually referred to as *C*- and *P*-metallaphosphaalkenes, respectively, constitute the vast majority of known metallaphosphaalkenes published to date.¹³⁹

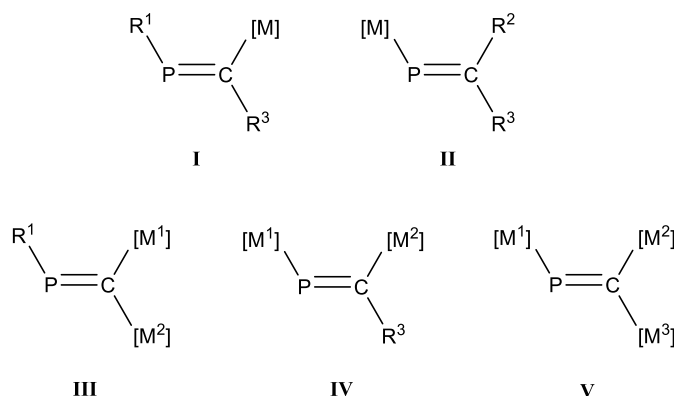
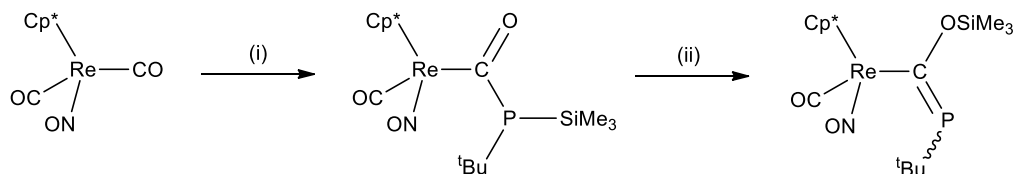


Figure 7: Five postulated metallaphosphaalkene types

1.2.3.1 Synthesis and characterization of *C*-metallaphosphaalkenes

The first example of a ‘type **I**’ *C*-metallaphosphaalkene was synthesised by reacting the lithium phosphide $\text{LiP}^t\text{Bu}(\text{SiMe}_3)$ with $[\text{Cp}^*\text{Re}(\text{CO})_2(\text{NO})][\text{BF}_4]$, generating the phosphine species $[\text{Cp}^*(\text{CO})(\text{NO})\text{Re}-\text{C}(\text{O})\text{P}^t\text{Bu}(\text{SiMe}_3)]$ *via* nucleophilic attack of a carbonyl group. Subsequently, upon warming to 40 °C, a 1,3-silyl shift furnished the phosphaaalkenyl complex $[\text{Cp}^*(\text{CO})(\text{NO})\text{Re}-\text{C}(\text{OSiMe}_3)=\text{P}^t\text{Bu}]$ (Scheme 19).¹⁴⁰ Formation of the $\text{Re}-\text{C}=\text{P}$ fragment was confirmed by $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy, with carbon resonances associated with the SiMe_3 group showing spin–spin coupling consistent with a 4-bond separation (δ_{C} 1.87 ($^4J_{\text{PC}} = 8.4$ Hz)). Progress of the reaction was monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy and a resonance at δ_{P} 43.2, assigned to the intermediate phosphine species, was seen to diminish upon

warming with the appearance of another singlet at δ_P 240.1, assigned to the metallaphosphaalkene. However, upon further warming and over the course of several hours, this resonance was seen to disappear with concomitant appearance of a resonance at δ_P 272.8. The reduced shielding of the P=C phosphorus centre was thought to be a result of rearrangement to the *Z*-isomer from the *E*-isomer; these data were the first indication that the chemical environment of the phosphorus centre in both *C*-metallated phosphaakenyls and the free phosphaaalkene are very similar.

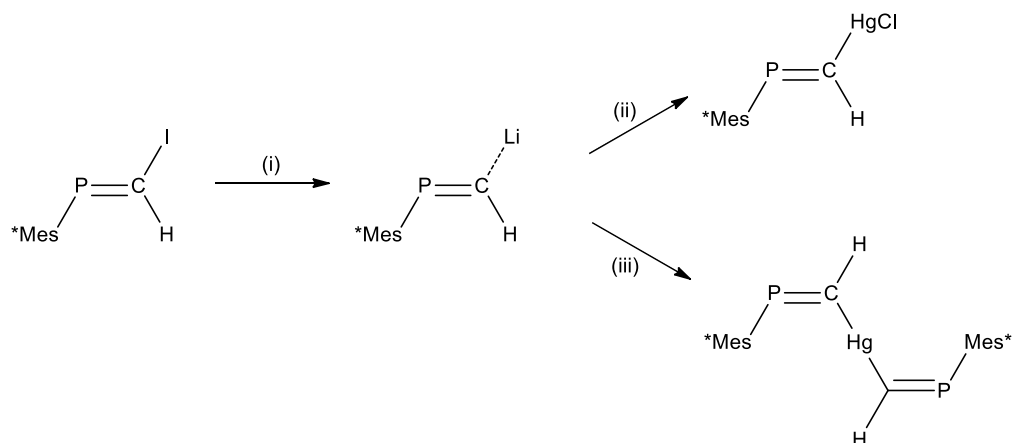


Scheme 19: Synthesis of the first *C*-metallaphosphaalkene. *Reagents and Conditions:* (i)

$\text{LiP}(\text{SiMe}_3)^t\text{Bu}$, Et_2O , -78°C ; (ii) 20°C , 30 min.¹⁴⁰

With this method of phosphaaalkene formation relying on the availability of bulky lithiated phosphines, alternative approaches were developed using *C*-halogenophosphaalkenes, exploiting the known propensity of compounds of the type $\text{RP}=\text{CX}_2$ to undergo oxidative addition to a metal. However, again, this method is limited by the ability to obtain precursors of the type $\text{RP}=\text{CX}_2$. The *C*-halogenophosphaalkenes that have been isolated generally require sterically encumbering functional groups or strongly electron withdrawing groups such as fluoromethyl derivatives on the phosphorus atom. A rare exception to this is $\text{MeP}=\text{CF}_2$, synthesised upon addition of CF_2Br_2 to $\text{MeP}(\text{SiMe}_3)_2$; however, $\text{MeP}=\text{CF}_2$ undergoes dimerization, furnishing $(\text{MePCF}_2)_2$.¹⁴¹

C-Halogenophosphaalkenes have also been used to access lithiophosphaalkenes, which can be synthesised by reaction of the former with an excess of $^n\text{BuLi}$ (Scheme 20), but tend to be thermally unstable and as such are often generated at low temperature and used *in situ*.¹⁴² An example of this is the reaction of $\text{Mes}^*\text{P}=\text{CHLi}$ (a mixture of *E/Z*-isomers in an 80:20 ratio) with 1 equivalent of HgCl_2 , yielding the mercurio-phosphaalkene $[\text{ClHgCH}=\text{PMes}^*]$.¹⁴³ When using 0.5 equivalents of HgCl_2 , the anticipated bis(phosphaalkenyl)mercury derivative is generated, with both *EE*- and *ZZ*-isomers observed through ^{31}P NMR spectroscopy in an 80:20 ratio. It was also noted that the *EE*-isomer underwent rearrangement to the *ZZ*-isomer or decomposed over time. The *ZZ*-isomer was further characterised by X-ray diffraction studies.

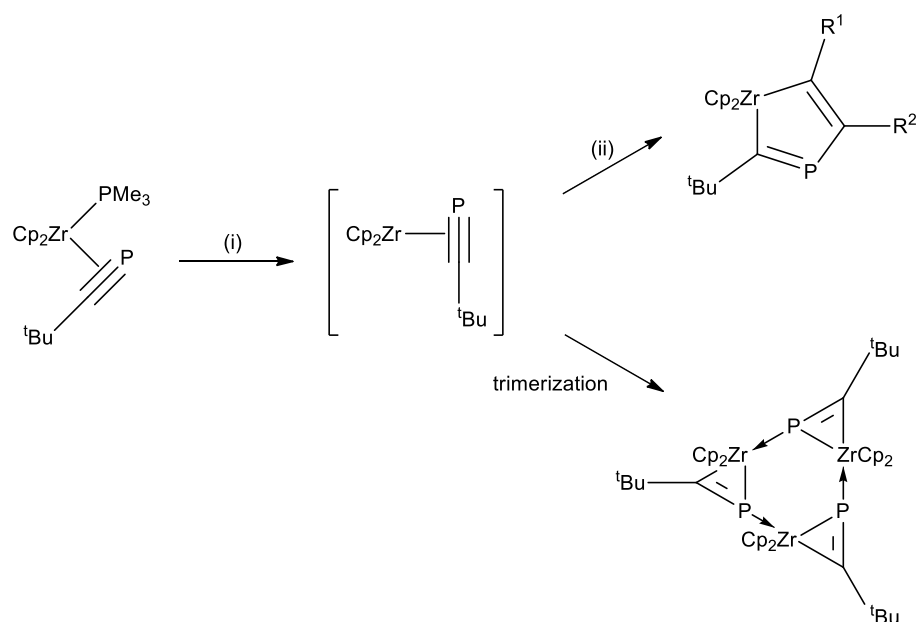


Scheme 20: Synthesis of C-mercuriophosphaalkenes *via* a C-lithiophosphaalkene. *Reagents and Conditions:* (i) $^n\text{BuLi}$, THF, 30 min, $-80\text{ }^\circ\text{C}$; (ii) HgCl_2 ; (iii) $\frac{1}{2} \text{HgCl}_2$.

Similar reactivity has since been observed with C-metallaphosphaalkenes functionalized by p-block metals. A notable example is that reported by Escudié in 1996,¹⁴⁴ wherein the C-lithiophosphaalkene $\text{Mes}^*\text{P}=\text{CBrLi}$ was quenched with the difluorogermane $\text{Mes}^*_2\text{GeF}_2$ to afford $[\text{Mes}^*_2\text{FGe}-\text{CBr}=\text{PMes}^*]$. This methodology has even been extended beyond phosphorus to other group 15 elements such as arsenic, whereby compounds of the type $\text{RAs}=\text{CXH}$ have been synthesised *via* lithio-carbenoids;¹⁴⁵ such examples highlight the wide applicability of lithiated group 15 heteroalkenes in synthetic chemistry.

C-Magnesiophosphaalkenes offer a somewhat more flexible approach compared to their lithium counterparts. Addition of RMgX to a phosphalkyne ($\text{R}'-\text{C}\equiv\text{P}$) furnishes compounds of the type $\text{RP}=\text{CR}'\text{MgX}$, similar to those reported by Jones and co-workers.¹⁴⁶ This is advantageous as it enables the generation of a wider range of compounds due to the R group originating from a preformed Grignard reagent as opposed to the parent phosphalkyne, which are more unstable and less readily available.

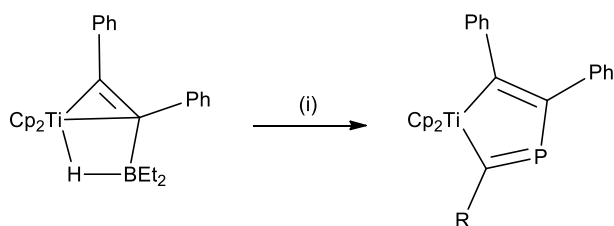
Phosphaalkynes have also been employed in the pursuit of C-metallaphosphaalkenes without the need for Grignard-type conditions. Cyclodimerization of alkynes with phosphalkynes within the coordination sphere of transition metals generate C-metallated heterocycles incorporating the 'C=P' moiety. An example of this is the zirconium complex $[\text{Cp}_2\text{Zr}(\eta^2-\text{P}\equiv\text{C}^t\text{Bu})(\text{PMe}_3)]$, which undergoes cycloaddition with various alkynes generating a heterocyclic complex. Alternatively, without the presence of a secondary alkyne, $^t\text{BuC}\equiv\text{P}$ will trimerize with itself, with each $\text{P}=\text{C}$ carbon centre exhibiting a σ -bond with a Zr centre and η^1 -coordination to a second Zr centre (Scheme 21).¹³⁸



Scheme 21: Heterocyclic C-metallated phosphalkenes *via* an η^2 -coordinated phosphalkyne.

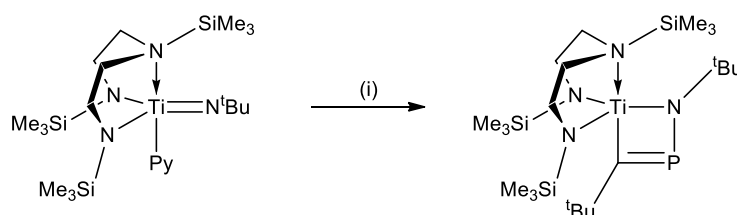
Reagents and Conditions: (i) BEt_3 ; (ii) $\text{R}^1\text{C}\equiv\text{CR}^2$ ($\text{R}^1/\text{R}^2 \neq \text{SiR}_3$).¹³⁸

The heterocyclic compounds $[\text{Cp}_2\text{Ti}(\text{PhC}=\text{CPh})(\mu\text{-C}(\text{R})=\text{P})]$ ($\text{R} = \text{tBu}, \text{Ad}$) have also been synthesised but *via* an alternative route, *i.e.* addition of $\text{tBuC}\equiv\text{P}$ to the complex $[\text{Cp}_2\text{Ti}(\text{PhC}=\text{CPh})(\mu\text{-H})(\text{BEt}_2)]$ with loss of HBEt_2 and formation of the $\text{Ti}-\text{C}=\text{P}$ moiety.¹⁴⁷



Scheme 22: Heterocyclic compounds incorporating the $\text{C}=\text{P}$ moiety, formed within the coordination sphere of the Ti centre ($\text{R} = \text{Ad}, \text{tBu}$). *Reagents and Conditions:* (i) $2 \text{ RC}\equiv\text{P}$, pentane, 2 h.¹⁴⁷

An alternative approach to furnish a C-metallated heterocycle utilising $\text{tBuC}\equiv\text{P}$ was demonstrated by Cloke *et al.* in 1999, with a $[2+2]$ cycloaddition of $\text{tBuC}\equiv\text{P}$ and a $\text{Ti}=\text{N}$ bond furnishing the cycloadduct $[\text{Ti}\{\text{N}(\text{SiMe}_3)[\text{CH}_2\text{CH}_2\text{N}(\text{SiMe}_3)_2]\}(\text{P}=\text{C}^{\text{tBu}}\text{N}^{\text{tBu}})]$, which exhibits a phosphorus resonance at *ca.* $\delta_{\text{P}} 209$ in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum assigned to the $\text{C}=\text{P}$ bond (Scheme 23).¹⁴⁸

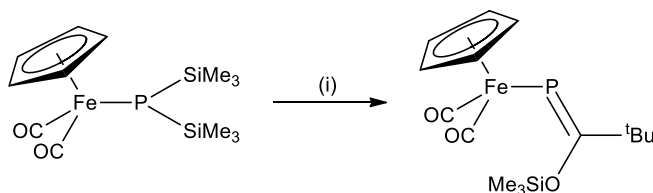


Scheme 23: Phosphaalkyne–imido [2+2] cycloaddition furnishing a C-metallaphosphaalkene.

Reagents and Conditions: (i) $t\text{BuC}\equiv\text{P}$, C_6H_6 , 48 h, r.t.¹⁴⁸

1.2.3.2 Synthesis and Characterization of P-metallaphosphaalkenes

The first *P*-metallaphosphaalkene (type **II** structure), was the iron complex $[\text{Cp}(\text{CO})_2\text{Fe}-\text{P}=\text{C}(\text{OSiMe}_3)(t\text{Bu})]$.¹⁴⁹ Extrapolating from Becker's method of phosphaalkene formation, Weber reacted $[\text{CpFe}(\text{CO})_2(\text{P}(\text{SiMe}_3)_2)]$ and $t\text{BuC}(\text{O})\text{Cl}$, with subsequent elimination of Me_3SiCl , yielding the desired product shown in Scheme 24. A $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed a resonance at *ca.* δ_{P} 210, similar to that exhibited by the *C*-metallaphosphaalkenes, with X-ray diffraction data revealing a $\text{P}=\text{C}$ bond length of 1.70 Å confirming the formation of the phosphaalkenyl moiety. A *Z*-configuration about the $\text{P}=\text{C}$ bond was concluded from X-ray diffraction data.



Scheme 24: A *P*-metallaphosphaalkene with the $\text{P}=\text{C}$ bond formed within the coordination sphere of iron. *Reagents and Conditions:* (i) $t\text{BuCOCl}$, THF, 35 °C, 1 h.

An alternative method of *P*-metallaphosphaalkene synthesis is the addition of a *P*-functionalised phosphaalkene to a metal centre. An example of this is the facile synthesis of $[\text{CpM}(\text{CO})_3(\text{P}=\text{C}(\text{SiMe}_3)_2)]$ ($\text{M} = \text{Mo}, \text{W}$), demonstrated by Niecke¹⁵⁰ and co-workers and achieved by the addition of $\text{ClP}=\text{C}(\text{SiMe}_3)_2$ to a sodium carbonyl–metallate of the type $\text{Na}[\text{CpM}(\text{CO})_3]$. This work was of particular note as the phosphorus resonances were found to be highly deshielded (δ_{P} 505–589) and demonstrated for the first time that the polarity of a phosphaalkenyl could be inverted to yield a δ^- phosphorus centre. This was confirmed by addition of $\text{CF}_3\text{SO}_3\text{H}$ to $[\text{CpW}(\text{CO})_3(\text{P}=\text{C}(\text{SiMe}_3)_2)]$, furnishing the protonated species

[CpW(CO)₃(P(H)=C(SiMe₃)₂)]. It was believed that the σ -donating properties of the transition metal resulted in destabilisation of the lone pair, causing the P=C moiety to display ‘carbene’ rather than ‘alkene’-like reactivity.¹⁵⁰ In the same year, Arif *et al.* extended the idea of adding a *P*-functionalised phosphalkene to a metal centre and synthesised the first complex containing two phosphalkenyl fragments, [(μ_2 -P=C(SiMe₃)₂)₂Fe₂(CO)₆]. The two P=C moieties bridge the two metal centres, with σ -bonding to one Fe centre and η^1 -coordination to a second, again demonstrating the carbene-like reactivity of metalla-phosphaalkenyls (Figure 8).¹⁵¹ One phosphorus resonance for the two equivalent phosphorus centres was observed at δ_P 452.6, again showing a highly deshielded resonance and indicative of a *P*-metallaphosphaalkenyl fragments.

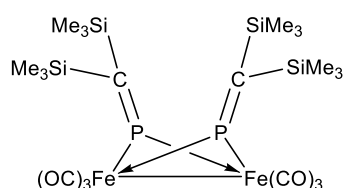
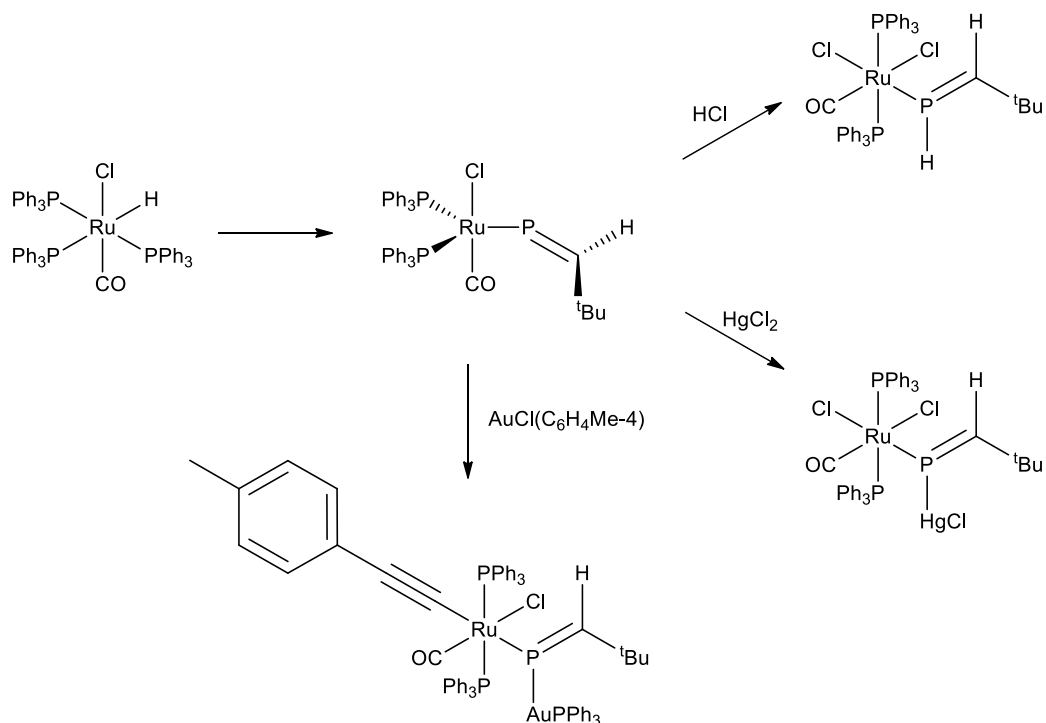


Figure 8: Bridging phosphaalkenyls demonstrating both σ -bonding and η^1 -coordination of the phosphorus centres to the Fe centres.

Another example of addition of a *P*-functionalised phosphalkene to a metal is the formation of [Cp*(CO)₂Fe(P=C(Ar)(NMe₂))], synthesised upon addition of Me₃SiP=C(Ar)(NMe₂) to [Cp*(CO)₂FeX] (X = Cl, Br), with subsequent loss of ClSiMe₃. This amino-substituted phosphalkenyl again demonstrates an inversion of polarity (*i.e.* P^{δ-}=C^{δ+}). In this case, it was found that the cause of this inversion was the ability of the nitrogen lone pair to interact with the π -system of the P=C bond, giving rise to ‘pseudo-allyl’ type conjugation. Phosphorus resonances for the resultant phosphalkenes were observed in the range δ_P 225–256 in their respective ³¹P{¹H} NMR spectra.^{124,152}

P-Metallaphosphaalkenes can also be synthesised by the reduction of a phosphalkyne within the coordination sphere of a metal, as demonstrated by Nixon *et al.* in 1991.¹⁵³ Attempts to crystallise [FeH(dppe)₂(P≡C(^tBu))][BF₄] from CH₂Cl₂ led to formation of the η^1 -ligated phosphalkene [FeH(dppe)₂(PF=CH(^tBu))][FeCl₂F₂] as a result of nucleophilic attack at the P≡C phosphorus centre by F⁻. Furthermore, treatment of [FeH(dppe)₂(P≡C(^tBu))][BF₄] with step-wise addition of two equivalents of HF furnished [FeH(dppe)₂(PF=CH(^tBu))][BF₄], followed by [FeH(dppe)₂(PF₂-CH₂(^tBu))][BF₄], demonstrating that in this case, the P=C bond has retained the parent metallaphosphaalkynyl’s polarity, with the phosphorus centre being electrophilic.¹⁵⁴

Another approach was that demonstrated by Hill *et al.* with the formation of the ruthena-phosphaalkene $[\text{RuCl}(\text{CO})(\text{PPh}_3)_2(\text{P}=\text{CH}(\text{tBu}))]$ *via* hydorruthenation of a phosphalkyne.¹⁵⁵ Addition of $\text{tBuC}\equiv\text{P}$ to a solution of $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ in DCM furnished the phosphaalkenic product in >90% yield (Scheme 25), with the reaction believed to proceed *via* a 1,2-addition of $\text{Ru}-\text{H}$ across the $\text{C}\equiv\text{P}$ bond. An interest in the addition of ligands to this coordinatively unsaturated species demonstrated that again, the polarity of the $\text{P}=\text{C}$ bond is reversed; addition of HCl led to electrophilic attack at the $\text{P}=\text{C}$ phosphorus centre, with addition of Cl^- to the metal, yielding the neutral, 6-coordinate species $[\text{RuCl}_2(\text{CO})(\text{PPh}_3)_2(\text{PH}=\text{CH}(\text{tBu}))]$. A range of heterodinuclear metallaphosphaalkenes were subsequently synthesised including $[\text{RuCl}_2(\text{CO})(\text{PPh}_3)_2(\text{P}(\text{HgCl})=\text{CH}(\text{tBu}))]$ and the alkynyl complex $[\text{RuCl}(\text{C}\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})(\text{PPh}_3)_2(\text{P}(\text{AuPPh}_3)=\text{CH}(\text{tBu}))]$, demonstrating for the first time the ability of the $\text{P}=\text{C}$ bond to undergo 1,2-addition across a metal–halide or metal–carbon bond (Scheme 25).¹⁵⁶ Such compounds exhibit an upfield shift in the $\text{P}=\text{C}$ phosphorus resonance to *ca.* δ_{p} 300 compared to that of the parent metallaphosphaalkene (*ca.* δ_{p} 450). Recently, Hayes *et al.* synthesised a similar *P*-metallaphosphaalkene, $[\text{Cp}^*(\text{iPr}_3\text{P})(\text{H})\text{Os}\equiv\text{Si}(\text{Trip})(\text{P}=\text{C}^{\text{tBu}})][\text{HB}(\text{C}_6\text{F}_5)_3]$, *via* a [2+2] cycloaddition of $\text{tBuC}\equiv\text{P}$ and the osmium silylyne $[\text{Cp}^*(\text{iPr}_3\text{P})(\text{H})\text{Os}\equiv\text{Si}(\text{Trip})][\text{HB}(\text{C}_6\text{F}_5)_3]$ ($\text{Trip} = 2,4,6\text{-iPr}_3\text{C}_6\text{H}_2$).¹⁵⁷



Scheme 25: Hydorruthenation yielding an η^1 -*P*-metallophosphaalkene with subsequent electrophilic addition at the phosphorus centre.

1.3 PHOSPHAALKYNES

1.3.1 SYNTHESIS OF ORGANO-PHOSPHAALKYNES

Few syntheses of organo-phosphaalkynes currently exist with even fewer regularly employed. Again, Becker was the major innovator of this work, providing the first facile synthesis of a phosphaalkyne, ${}^t\text{BuC}\equiv\text{P}$.^{71,158} This was achieved by base (NaOH) induced elimination of hexamethyldisiloxane from $(\text{Me}_3\text{Si})\text{P}=\text{C}({}^t\text{Bu})(\text{OSiMe}_3)$. This method has since been employed in the formation of a diverse range of $\text{R}-\text{C}\equiv\text{P}$ compounds where R can be a variety of species, from bulky aromatic groups¹⁵⁹ to small alkyl groups.^{66,85} However, ${}^t\text{Bu}-\text{C}\equiv\text{P}$ is more commonly used due to its greater stability compared to analogous compounds. A particularly interesting variation of this method was outlined by Cummins *et al.*,¹⁶⁰ with addition of pivaloyl chloride to the niobium complex $[\text{P}=\text{Nb}(\text{N}(\text{Np})\text{Ar})_3][\text{Na}(\text{THF})_x]$ (Np = neopentyl and Ar = 3,5- $\text{Me}_2\text{C}_6\text{H}_3$) leading to the synthesis of ${}^t\text{BuC}\equiv\text{P}$ within the coordination sphere of Nb *via* a phosphaalkenyl intermediate, with formation of $[\text{O}=\text{Nb}(\text{N}(\text{Np})\text{Ar})_3]$.¹⁶¹

A notable and common method for phosphaalkyne synthesis is *via* double dehydrohalogenation, which was initially carried out by flash pyrolysis of RCH_2PCl_2 compounds; however, this required very high temperatures and reduced pressure.^{66,162} Synthesis of $\text{F}-\text{C}\equiv\text{P}$ by Nixon and Kroto¹⁶³ demonstrated for the first time that step-wise elimination of HX from RCH_2PCl_2 compounds could be achieved by passing gaseous RCH_2PCl_2 across KOH pellets under reduced pressure. Double dehydrohalogenation of such species has since been refined, with more facile methods employed such as addition of two equivalents of both AgOTf (to remove the halide) followed by DABCO for deprotonation under mild conditions.^{38,164}

1.3.2 COORDINATION COMPOUNDS OF PHOSPHAALKYNES

Phosphaalkynes can coordinate to a metal centre through both the phosphorus lone-pair in an η^1 - fashion or more commonly, due to the higher energy of the π -system, through the $\text{C}\equiv\text{P}$ bond in an η^2 - fashion. A third and less frequently observed bonding mode combines coordination through the lone pair and through the π -system in a bimetallic system.¹⁶⁵

The first example of an η^2 -coordinated phosphaalkyne was published in 1981 by Nixon and co-workers.¹⁶⁶ The compound $[(\text{PPh}_3)_2\text{Pt}(\text{P}\equiv\text{C}{}^t\text{Bu})]$ was synthesised *via* addition of ${}^t\text{BuC}\equiv\text{P}$ to a solution of $[\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]$ in benzene, with subsequent loss of ethene. A ${}^{31}\text{P}\{^1\text{H}\}$ NMR spectrum exhibited multiplet resonances at δ_{P} 112.2 (${}^1J_{\text{PtP}} = 3587$ Hz), 114.7 (${}^1J_{\text{PtP}} = 3206$ Hz) and 56.9 (${}^1J_{\text{PtP}} = 62$ Hz) with the latter assigned to the $\text{P}\equiv\text{C}$ phosphorus centre. X-ray diffraction

studies revealed a particularly long $\text{P}\equiv\text{C}$ bond length of 1.672(17) Å compared to that of ${}^t\text{BuC}\equiv\text{P}$ (1.536(2) Å)¹⁶⁷ due to back-bonding from the metal d-orbitals into the $\text{P}\equiv\text{C}$ π^* -orbitals, with evidence to support this having since been established *via* computational studies.¹⁶⁸ Two further platinum complexes of similar structure were also published shortly thereafter, $[\text{Pt}(\text{dppe})_2(\text{P}\equiv\text{C}{}^t\text{Bu})]$ and $[\text{Pt}(\text{triphos})(\text{P}\equiv\text{C}{}^t\text{Bu})]$, all exhibiting similar structural properties, with long $\text{C}\equiv\text{P}$ bond lengths (*ca.* 1.70 Å) and high field phosphorus resonances below δ_{P} 50.^{169,170} Titanium and zirconium compounds bearing an η^2 -phosphaalkyne were later developed by Binger *et al.*⁶⁶ of the type $[\text{Cp}_2\text{M}(\text{PMe}_3)(\text{P}\equiv\text{C}{}^t\text{Bu})]$, *via* addition of ${}^t\text{BuC}\equiv\text{P}$ to $[\text{Cp}_2\text{M}(\text{PMe}_3)_2]$ and displacement of a PMe_3 ligand.

A more recent example was published by Jones and co-workers, with the synthesis of the bis-phosphaalkyne complex $[\{(\text{PPh}_3)_2\text{Pt}\}_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-P}\equiv\text{CC}(\text{C}_6\text{H}_4)_3\text{CC}\equiv\text{P})]$, with two η^2 -coordinated $\text{C}\equiv\text{P}$ fragments (Figure 9).¹⁷¹ Again, ${}^{31}\text{P}\{^1\text{H}\}$ NMR and X-ray diffraction data were consistent with those previously observed for η^2 -coordination (δ_{P} 94.9; d_{CP} = 1.681(13) Å).

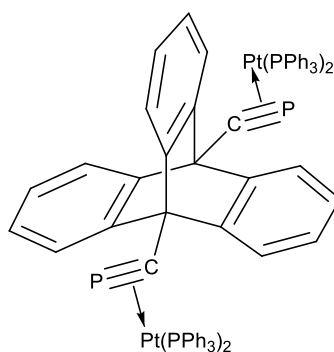
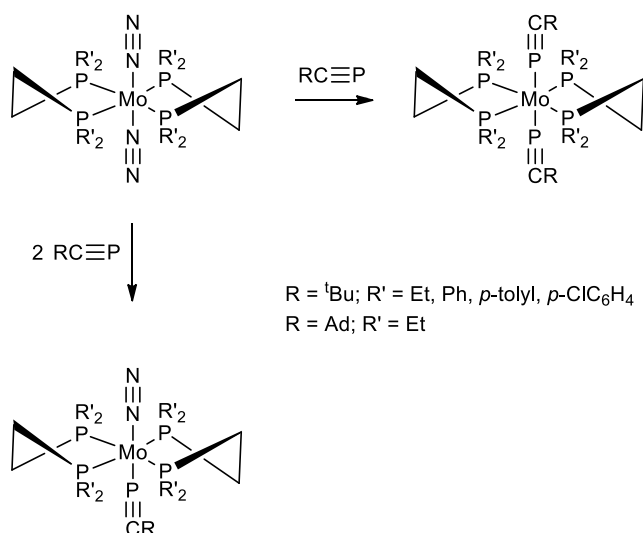


Figure 9: A diphosphaalkyne bridging two Pt complexes.¹⁷¹

Compounds bearing an η^1 -coordinated phosphaalkyne have only been successfully synthesised with substantial steric bulk about the metal centre, otherwise η^2 -coordination occurs preferentially. Phosphaalkynes displaying η^1 -coordination were first developed by Nixon *et al.*¹⁷² upon displacement of N_2 by $\text{R}-\text{C}\equiv\text{P}$ within compounds of the type $[\text{Mo}(\text{R}'_2\text{PC}_2\text{H}_4\text{PR}'_2)_2(\text{N}_2)_2]$ (Scheme 26). The sterically bulky bis-phosphine ligands in this case create a cavity into which $\text{R}-\text{C}\equiv\text{P}$ can insert, whilst providing sufficient steric bulk to protect the phosphaalkyne from further reaction. The $\text{P}\equiv\text{C}$ bond lengths of the bis-phosphaalkyne complex $[\text{Mo}(\text{depe})_2(\eta^1\text{-P}\equiv\text{C}(\text{Ad}))_2]$ were found to be *ca.* 1.52 Å, slightly shorter than that of free $\text{R}-\text{C}\equiv\text{P}$ compounds such as ${}^t\text{BuC}\equiv\text{P}$ (*ca.* 1.54 Å).¹⁷³ P–C phosphorus resonances were observed in the range δ_{P} –16.9 to 10.0 in ${}^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the resultant compounds.



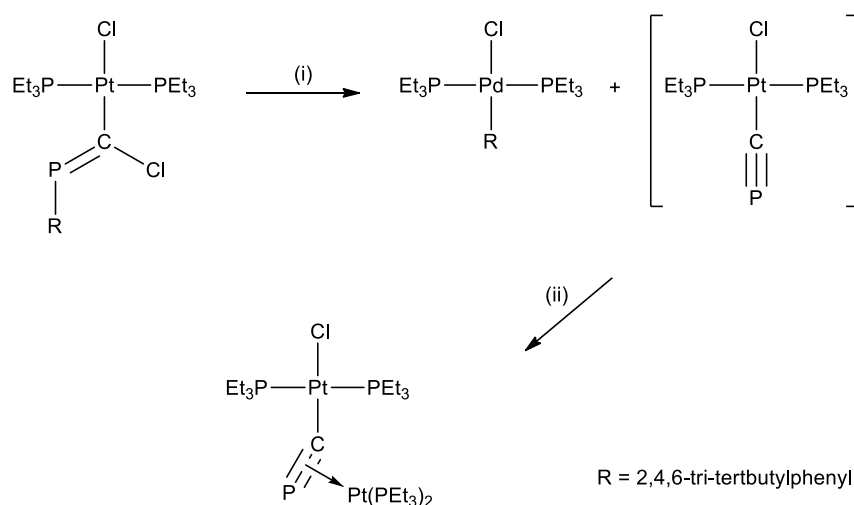
Scheme 26: First examples of η^1 -coordinated phosphalkyne compounds.¹⁷²

More recently, Russell and co-workers have developed analogous compounds employing the same preparative method, using the silyl-phosphalkyne $\text{P}\equiv\text{CSiMe}_3$ to synthesise $[\text{Mo}(\text{dppe})_2(\text{P}\equiv\text{CSiMe}_3)_2]$.¹⁷⁴ X-Ray diffraction studies confirmed that the $\text{C}\equiv\text{P}$ bond length (1.540(2) Å) was again close to that of a free phosphalkyne. Interestingly, unlike Nixon's analogous Mo compounds, $[\text{Mo}(\text{dppe})_2(\text{P}\equiv\text{CSiMe}_3)_2]$ exhibited a highly deshielded phosphorus resonance at δ_{P} 171.7, which is possibly due to the difference in the $\text{P}\equiv\text{CR}$ unit, with R in this case being a silicon rather than carbon-centered substituent. This is also reflected in the phosphorus shifts of the free phosphalkynes (δ_{P} 99.4 ($\text{P}\equiv\text{CSiMe}_3$); δ_{P} 69.2 ($\text{P}\equiv\text{C}^t\text{Bu}$)).

Other such complexes have been demonstrated by Grützmacher and co-workers, who synthesised Ru and Fe hydrido complexes of the type $[\text{MH}(\text{dppe})_2(\text{P}\equiv\text{CPh}_3)][\text{OTf}]$ by addition of $\text{P}\equiv\text{CPh}_3$ to the respective $[\text{MH}(\text{dppe})_2][\text{OTf}]$ complex.¹⁷⁵ Resonances at δ_{P} 0.94 and -27.3 for the Fe and Ru compounds, respectively, were observed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy of these compounds, with the Fe analogue possessing a $\text{C}\equiv\text{P}$ bond length of 1.535(2) Å.¹⁷⁶ Grützmacher later extended this method to the silyl analogue $[\text{RuH}(\text{dppe})_2(\text{P}\equiv\text{CSiPh}_3)][\text{OTf}]$.¹⁷⁷ A $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the η^1 -bound phosphalkyne complex presented a quintet at δ_{P} 143.8 ($J_{\text{PP}} = 27.8$ Hz). Similar to Russell's silyl-phosphalkyne compounds, this phosphorus resonance is highly deshielded compared to the carbon-based analogues demonstrated by Nixon. In addition, a $\text{P}\equiv\text{C}$ bond length of 1.520(3) Å was observed, typical of that seen for η^1 -phosphalkynes.

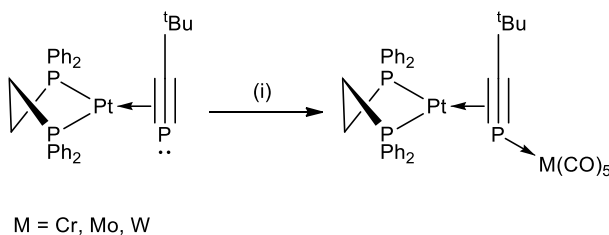
Phosphalkynes, like phosphalkenes, can also be formed within the coordination sphere of a metal centre. This is exemplified by the work of Angelici *et al.*, who demonstrated the synthesis of the first bridging cyaphide ($-\text{C}\equiv\text{P}$) complex.^{178,179} Stepwise addition of $[\text{Pd}(\text{PET}_3)_4]$ and

[Pt(PEt₃)₄] to [PtCl(PEt₃)₂(C(Cl)=PR)] led to formation of a cyaphide ligated Pt transition complex, with subsequent coordination of the C≡P moiety to a second Pt centre (Scheme 27). A C≡P phosphorus resonance was observed at δ_P 107.0, while X-ray diffraction studies revealed a C≡P bond length of 1.666 (6) Å, longer than that of a free phosphalkyne but consistent with that previously observed for η^2 -coordination. This bridging phosphalkyne was later converted to a number of trinuclear metal–cyaphide complexes, wherein the phosphorus lone pair coordinates in an η^1 -fashion to a third metal centre.¹⁸⁰ This was achieved by addition of complexes of the type ML_n (ML_n = [W(CO)₅]·THF, [PtCl₂(PEt₃)₂]), yielding the desired complexes [Cl(Et₃P)₂Pt[μ^1 - η^1 , η^1 , η^2 -C≡P{ML_n}]Pt(PEt₃)₂].¹⁸¹



Scheme 27: First example of the cyaphide ligand formed *in situ*. *Reagents and Conditions:* (i) Pd(PEt₄), C₆H₆, 8 h, r.t.; (ii) Pt(PEt₄), C₆H₆, 30 min, r.t.

Phosphaalkynes can undergo η^1 -coordination to a metal centre whilst also binding to a second metal centre in an η^2 -fashion, again demonstrated by Angelici *et al.*¹⁸² The complexes [Pt(dppe)(μ - η^2 : η^1 -P≡C^tBu)M(CO)₅] were prepared by addition of [M(CO)₅·(THF)] (M = Cr, Mo, W) to a solution of [Pt(dppe)(η^2 -P≡C^tBu)] in THF and exhibited η^2 -coordination to the platinum centre and η^1 -coordination to the second metal centre through the phosphorus lone pair (Scheme 28). P=C phosphorus resonances were consistent with those of η^2 -bound phosphaalkynes and a predicted shift upfield of the P≡C phosphorus resonance on descending the group 6 metals was also observed (δ_P 99.0 (Cr); 76.7 (Mo); 46.3 (W)).

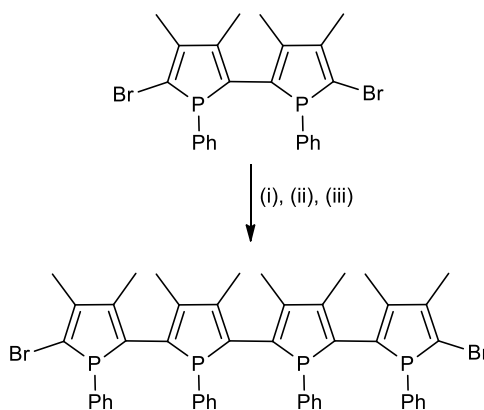


Scheme 28: Synthesis of the first $\eta^2:\eta^1$ -coordination compound of a phosphaaalkyne. *Reagents and Conditions:* (i) $[\text{Mo}(\text{CO})_5 \cdot (\text{THF})]$, THF, 12 h, r.t.¹⁸²

1.4 EXTENDED CONJUGATION IN LOW-COORDINATE PHOSPHORUS-CONTAINING MOLECULES

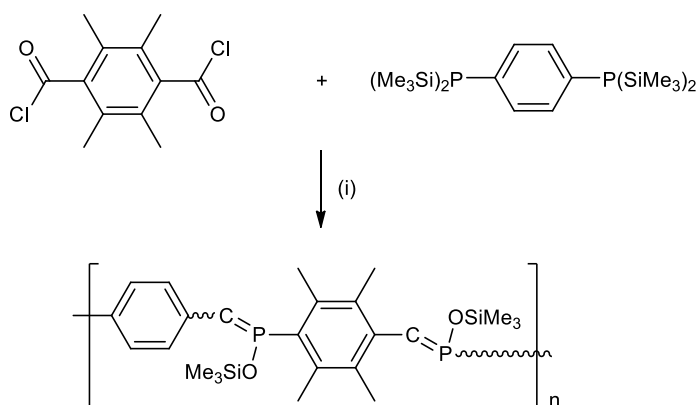
The field of low-coordinate phosphorus has recently been applied to that of molecules with extended π -conjugation, due to their electrical conductivity and potential application in areas such as photovoltaics, optics and semiconductors.^{183–186} While this work initially began with all-carbon polymer chains, it was soon established that doping with a main-group element with either a lone pair or a vacant orbital could significantly enhance the semiconducting properties of such molecules. Given the established carbon–phosphorus analogy, phosphorus has been studied extensively for its use in π -conjugated systems.^{184,187}

Phospholes have been the most widely studied of the organophosphorus materials for their use as π -conjugated systems. This is largely due to the pyramidal nature of the phosphorus centre leading to poor aromaticity due to reduced interaction between the phosphorus lone pair and the extended π -system. Additionally, $\sigma^*-\pi^*$ interactions between the P–R and butadiene moieties, respectively, result in a low-energy LUMO, which is an important factor for semi-conducting materials as it reduces the HOMO–LUMO bandgap, thereby facilitating electron transport.^{183,188} Preliminary work by Mathey and co-workers demonstrated the first phosphole chain incorporating four phosphole units upon coupling of two molecules of $(\text{C}_4\text{Me}_2\text{BrPPh})_2$ (Scheme 29);¹⁸⁹ however, the resultant product was a complex mixture of diastereomers.



Scheme 29: Synthesis of the first polyphosphole *via* copper-catalysed cross-coupling. *Reagents and Conditions:* (i) $n\text{BuLi}$, THF, $-90\text{ }^{\circ}\text{C}$; (ii) CuCl_2 , $-90\text{ }^{\circ}\text{C}$, 1 h; (iii) $25\text{ }^{\circ}\text{C}$, 2 h.¹⁸⁹

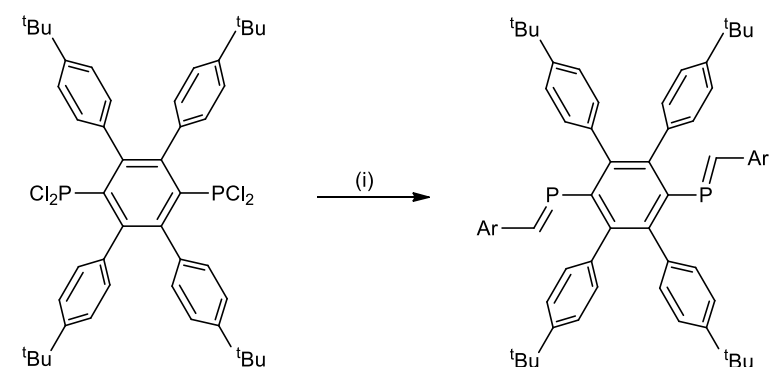
Phosphaalkenes have also been incorporated into π -conjugated systems, with Gates and co-workers synthesising poly(*p*-phenylenephosphaalkene) *via* the Becker condensation from two bifunctional reagents (Scheme 30).^{190,191} The resultant polymer exhibited broad multiplet resonances in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum in the ranges δ_{P} 157–149 and δ_{P} 138–124, attributed to the *E*- and *Z*-isomers, respectively. Shortly thereafter, Ott *et al.* developed oligoacetylenes devoid of aromatic fragments of the type $\text{Mes}^*\text{P}=\text{C}(\text{C}\equiv\text{C}(\text{iPr}_3\text{Si}))_2$ upon addition of Mes^*PCl_2 to $\text{ClCH}(\text{C}\equiv\text{C}(\text{iPr}_3\text{Si}))_2$,^{192–194} with a phosphorus resonance observed at *ca.* δ_{P} 330, similar to those observed by Yoshifuji and co-workers for analogous monomers.¹⁹⁵ A characteristic $\text{P}=\text{C}$ bond length of 1.68 \AA was also observed.



Scheme 30: Synthesis of poly(*p*-phenylenephosphaalkene) *via* the Becker condensation. *Reagents and Conditions:* (i) $85\text{ }^{\circ}\text{C}$, 8 h.^{190,191}

Protasiewicz and co-workers have also reported the synthesis of a $\text{P}=\text{C}$ containing π -system, extending their previously reported ‘Phospha-Wittig’ methodology to form $\text{P}=\text{C}$ bonds *in situ*.

Addition of Zn and PMe_3 to a bis(dichlorophosphine) complex (Scheme 31)¹⁹⁶ with subsequent addition of a suitable aldehyde furnished the desired diphosphaalkene complex. This work was later extended to synthesise $\text{P}=\text{C}$ -containing polymers from a bis(dichlorophosphine) and a dialdehyde.^{197,198} Despite the extensive studies on low-coordinate phosphorus-containing π -systems, there have been no reports on the organometallic chemistry of such systems or indeed, the incorporation of the $\text{C}\equiv\text{P}$ moiety into an extended π -system.



Scheme 31: The Phospha-Wittig reaction used to furnish an extended π -system incorporating $\text{P}=\text{C}$ ($\text{R} = \text{Ph}$, $2,6\text{-Cl}_2\text{C}_6\text{H}_3$). *Reagents and Conditions:* (i) Zn, PMe_3 , ArC(H)O , THF, 2 h.¹⁹⁶

1.5 CONCLUDING REMARKS

Since Dimroth's seminal work on low-coordinate phosphorus chemistry, a vast quantity of work has been carried out in the field with respect to both organo-phosphorus and organometallic phosphorus, which has led to a far greater understanding of multiple bonding and reactivity of elements beyond the first row of the periodic table. While much of the organometallic chemistry of low-coordinate phosphorus has focused on aromatic heterocycles such as the phosphinines and phospholides, there has also been much interest in the reactivity of phosphalkynes in organometallics and the synthesis of organometallic phosphalkenes.

However, there is still much scope for further investigation, particularly with regard to the incorporation of phosphorus into extended π -systems. While there have been a number of interesting studies in this area with respect to organo-phosphorus, little has been reported on the organometallic chemistry of such conjugated systems.

Herein, the chemistry of metalla-phosphaalkenyl/-phosphaalkynyl compounds is explored,

focusing on the synthesis of novel complexes and precursors, but also on the electronic properties and further reactivity of these unique species. Discussion initially focuses on the chemistry of ruthenaphosphaalkenyls, expanding on work by Hill and co-workers and discovering unanticipated reactivity of the P=C moiety. Efforts to produce a number of organometallic-acetylenes is then discussed, with some well-established carbon chemistry techniques used to install phosphorus-containing groups in the chain, alongside established techniques used in low-coordinate phosphorus chemistry for the synthesis of multiple P-C bonds. Finally, synthesis of the elusive cyaphide ligand and its incorporation into extended π -systems is discussed. Further reactivity of such complexes and their different bonding modes are also explored.

CHAPTER 2: INVESTIGATION INTO THE STRUCTURAL AND ELECTRONIC PROPERTIES OF RUTHENA-PHOSPHAALKENES AND THEIR CHEMISTRY

2.1 INTRODUCTION

A number of synthetic routes towards phosphalkenes have been developed since the 1960s, however, successful hydorruthenation of a $P\equiv C$ bond, akin to the chemistry of the $C\equiv C$ analogues, was not achieved until 1996; this seminal work published by Hill and Jones¹⁵⁵ led to formation of the *P*-metallaphosphalkenyl, $[RuCl(CO)(PPh_3)_2(P=CH^tBu)]$ (**1**) (*vide infra*). Phosphalkene formation *via* this method is somewhat hindered by the instability of most phosphalkyne reagents of the type $RC\equiv P$, with $^tBuC\equiv P$ being an exception to this. Nonetheless, a number of hydrometallation products have since been synthesised, such as the osmium complex $[OsCl(CO)(PPh_3)_2(P=CH(^tBu))]$.¹⁹⁹ The recent synthesis of the silyl-phosphalkynes $Me_3SiC\equiv P$ ³⁸ and $PhMe_2SiC\equiv P$ ²⁰⁰ has enabled the synthesis of two further analogues of **1**, $[RuCl(CO)(PPh_3)_2(P=CH(SiMe_3))]$ ¹⁶⁴ (**2**) and $[RuCl(CO)(PPh_3)_2(P=CH(SiMe_2Ph))]$ ^{*} (**3**), respectively.

Recent work in the field has focused on the subsequent reactivity of such compounds. Colleagues in the Crossley group have recently synthesised the *P*-pyrazolyl phosphalkene complex $[Ru(CO)\{\kappa^3\text{-}N,C,P\text{-}P(Pz^*)CH(SiMe_3)\}(PPh_3)_2]$ (**4**) upon reaction of KTp^* and $[RuCl(CO)(PPh_3)_2(P=CH(TMS))]$ (**2**) – a result of fragmentation of the trispyrazolylborate ion.[†] A complex series of multiplets was observed in a $^{31}P\{^1H\}$ NMR spectrum of the resultant product, with a large shift upfield demonstrating loss of the phosphalkenyl moiety; retention of $CH(SiMe_3)$ was observed through 1H NMR spectroscopy. X-Ray diffraction studies revealed a three-membered $Ru-P-C$ ring with a bridging pyrazolyl group. However due to the poor quality of these diffraction data, only connectivity could be reliably deduced, leaving ambiguity regarding the nature of the $Ru-P-C$ linkage.

In view of this interesting and unprecedented reactivity, further study into the precise structure of these compounds is warranted. Herein, the direct targeted synthesis of this compound and analogues is discussed. Mechanistic aspects of this reactivity have also been explored experimentally and theoretically, providing a better understanding of the nature of **1–3**.

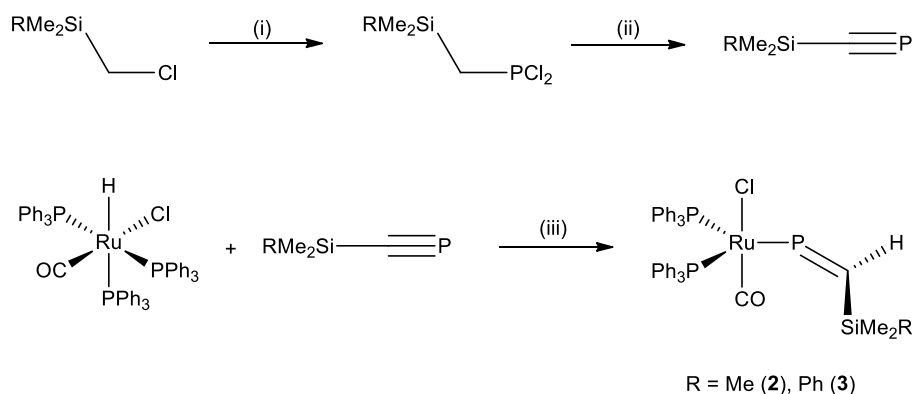
^{*} I.R. Crossley – unpublished results.

[†] V.K. Greenacre, MChem dissertation, Univ. Sussex, 2012.

2.2 SYNTHESIS AND STRUCTURE OF $[\text{Ru}(\text{CO})\{\kappa^3\text{-}N,C,P\text{-}P(\text{Pz}')\text{CH}(\text{R})\}(\text{PPh}_3)_2]$

2.2.1 SYNTHESIS OF $[\text{RuCl}(\text{CO})(\text{PPh}_3)_2(\text{P}=\text{CHR})]$ ($\text{R} = \text{SiMe}_3$ (**2**), SiMe_2Ph (**3**))

Compounds of the type $[\text{RuCl}(\text{CO})(\text{PPh}_3)_2(\text{P}=\text{CHR})]$ ($\text{R} = \text{SiMe}_3$ (**2**), SiMe_2Ph (**3**)) were prepared by modified literature procedures.^{38,164} A solution of $\text{RSiC}\equiv\text{P}$ was first prepared *via* double dehydrohalogenation of $\text{RSiCH}_2\text{PCl}_2$ by addition of 2 equivalents of AgOTf and DABCO in toluene. The solution was calibrated in d^6 -benzene against the fully relaxed resonance of PPh_3 ($d_1 = 50$ s) by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. To a stirring suspension of $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ was added a slight excess of the phosphalkyne solution. After 1 h, the solution was filtered and solvent removed under reduced pressure. The resultant product was washed with hexane, yielding an orange/yellow solid in good yield and characterised by $\text{P}=\text{C}$ phosphorus resonances at δ_{p} 544.4 and 553.9 for **2** and **3**, respectively (Scheme 32).



Scheme 32: Synthesis of **2** and **3** *via* the phosphalkynes $\text{P}\equiv\text{CSiMe}_2\text{R}$ ($\text{R} = \text{Me}, \text{Ph}$). *Reagents and Conditions:* (i) $\text{Mg}, \text{Et}_2\text{O}, \text{PCl}_3$, 16 h, -78°C ; (ii) AgOTf , DABCO, toluene, 1 h, r.t.; (iii) DCM, 1 h, r.t.

To date, there have been no reported X-ray diffraction studies of a ruthenaphosphaalkenyl; therefore, DFT studies were able to give some insight into the structure of compound **2**. The structure was optimized at the B3LYP level of theory with the LANL2DZ basis set for Ru and 6-31G** for all other atoms (Figure 10). Selected bond lengths and angles are detailed in Table 1 and discussed below. Interestingly, while relative Mulliken charges of **2** demonstrate a significant partial negative charge on the $\text{C}=\text{P}$ phosphorus centre, the LUMO of **2** appears to be heavily associated with the $\text{C}=\text{P}$ bond (Figure 11), with the HOMO centred about ruthenium. These data have implications for the reactivity of this molecule and give some insight into the ambiphilic activity at the phosphorus centre (*vide supra*).

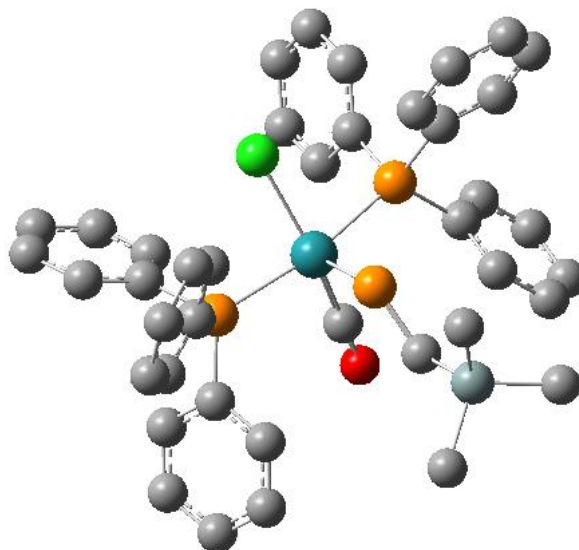


Figure 10: DFT-optimized structure of $[\text{RuCl}(\text{CO})(\text{PPh}_3)_2(\text{P}=\text{CHSiMe}_3)]$ (**2**). H atoms omitted for clarity.

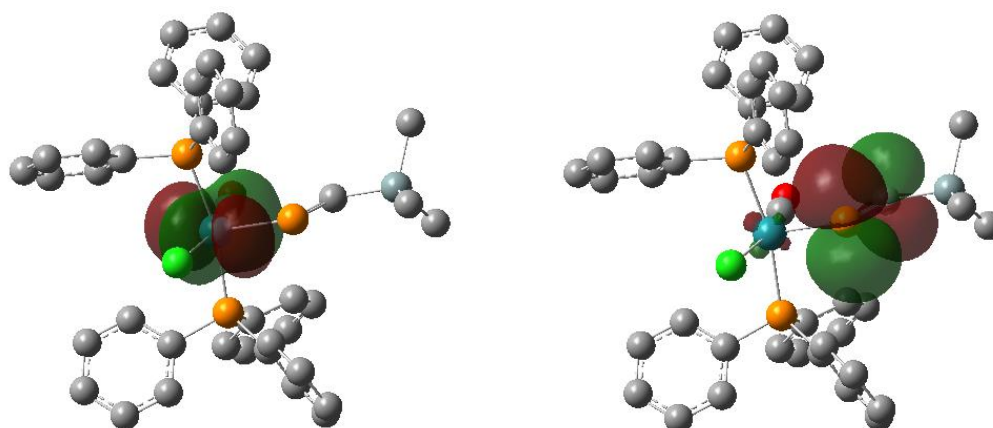


Figure 11: DFT-optimised structure of **2** showing the HOMO (left) and LUMO (right).

Since the completion of this work, crystals of **2** have been successfully grown by colleagues[‡] from a saturated solution in Et_2O at -20°C and analysed by X-ray diffraction studies, the data for which have been included here for comparison. The asymmetric unit consists of one molecule of the metallaphosphaalkene and two molecules of Et_2O (Figure 12). Both X-ray and DFT structures demonstrate a square-based pyramidal structure, with $\text{P}=\text{C}$ bond lengths of *ca.* 1.67 \AA , typical of that usually observed for metallaphosphaalkenes (Table 1).^{115,151,156} Calculated bond angles for the $\text{Ru}-\text{P}=\text{CH}(\text{SiMe}_3)$ fragment are in good agreement with X-ray diffraction

[‡]V. K. Greenacre – unpublished results.

data revealing Ru–P–C and P–C–Si angles of $124.4(4)^\circ$ and $122.5(7)^\circ$, respectively, compared with calculated values of 120.7° and 123.1° . However, some discrepancy does exist between that of the calculated and experimental values obtained, with Ru–C and Ru–P found to be somewhat shorter than that calculated.

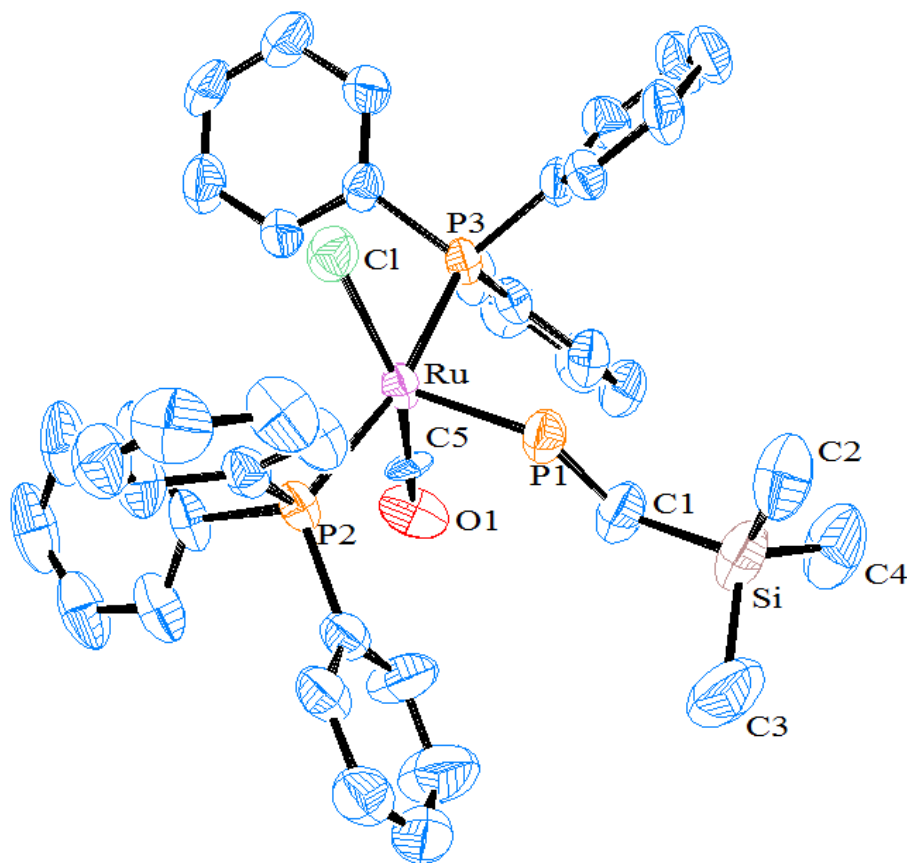


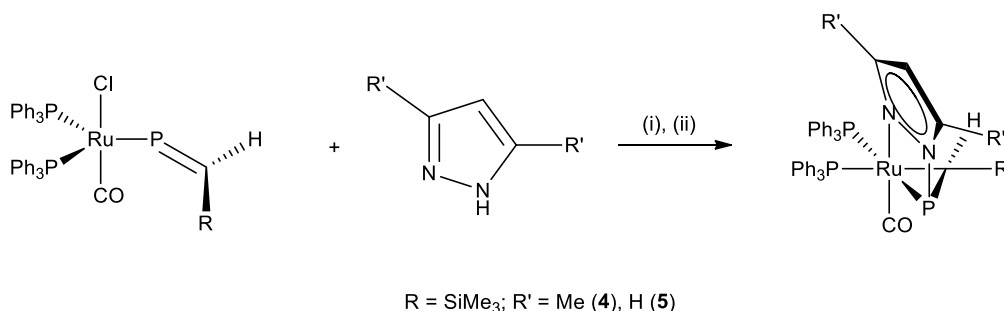
Figure 12: Molecular structure of one molecule of $[\text{RuCl}(\text{CO})(\text{PPh}_3)_2(\text{P}=\text{CHSiMe}_3)]$ (**2**), in crystals of Et_2O solvate. 50% thermal ellipsoids. H atoms omitted for clarity.

Table 1: Selected bond lengths (\AA) and angles ($^\circ$) for the X-ray and DFT optimised structures for compound **2**.

	X-ray	DFT
Ru(1)–C(5)	1.735(9)	1.852
Ru(1)–P(1)	2.226(2)	2.298
P(1)–C(1)	1.660(11)	1.677
Ru(1)–P(1)–C(1)	124.4(4)	120.7
P(1)–C(1)–Si(1)	122.5(7)	123.1

2.2.2 SYNTHESIS AND CHARACTERISATION OF $[\text{Ru}(\text{CO})\{\kappa^3\text{-}N,C,P\text{-}P(\text{Pz}^*)\text{CH}(\text{SiMe}_3)\}(\text{PPh}_3)_2]$

Direct synthesis of $[\text{Ru}(\text{CO})\{\kappa^3\text{-}N,C,P\text{-}P(\text{Pz}^*)\text{CH}(\text{SiMe}_3)\}(\text{PPh}_3)_2]$ (**4**) and $[\text{Ru}(\text{CO})\{\kappa^3\text{-}N,C,P\text{-}P(\text{Pz})\text{CH}(\text{SiMe}_3)\}(\text{PPh}_3)_2]$ (**5**) was achieved by initial lithiation of HPz' with $^n\text{BuLi}$ in THF under ambient conditions, followed by addition of the lithium pyrazolate to a solution of **2** (Scheme 33). The desired compounds were furnished within 1 h and extracted with DCM to remove excess LiCl .



Scheme 33: Synthesis of complexes **4** and **5**. *Reagents and Conditions:* (i) $^n\text{BuLi}$, THF, 10 min, r.t.; (ii) THF, 1 h, r.t.

Both complexes **4** and **5** demonstrated three multiplet resonances in their respective $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (**4**: δ_{P} 46.6 (d, $^2J_{\text{PP}} = 17.1$ Hz), 39.2 (dd, $^2J_{\text{PP}} = 49.7, 17.1$ Hz), 32.9 (d, $^2J_{\text{PP}} = 49.8$ Hz; **5**: δ_{P} 58.7 (d, $^2J_{\text{PP}} = 46.8$ Hz), 46.6 (d, $^2J_{\text{PP}} = 17.8$ Hz), 42.0 (dd, $^2J_{\text{PP}} = 46.8, 17.8$ Hz)). A large singlet resonance in the ^1H NMR spectrum of both compounds at *ca.* $\delta_{\text{H}} -1.0$, combined with a broad resonance at *ca.* $\delta_{\text{H}} 1.60$ (integrating 9:1 respectively) indicates retention of the $\text{CH}(\text{SiMe}_3)$ fragment; this is supported by a multiplet resonance observed in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, assigned to the CH carbon centre (**4**: δ_{C} 44.9 (ddd, $J_{\text{CP}} = 78.0, 32.0, 5.1$ Hz); **5**: δ_{C} 47.6 (ddd, $J_{\text{CP}} = 78.7, 31.3, 4.1$ Hz)). IR spectroscopy supported retention of the $\text{C}\equiv\text{O}$ ligand (*ca.* $\nu_{\text{CO}} 1907\text{ cm}^{-1}$) and bulk purity was confirmed by elemental analysis.

2.2.3 STRUCTURAL FEATURES OF COMPLEXES **4** AND **5**

Crystals of **5** were obtained by slow-cooling of a saturated CD_2Cl_2 solution (Figure 13, Table 2), showing two molecules of **5** in the asymmetric unit in different orientations. Figure 14 shows one molecule of **5** for clarity.

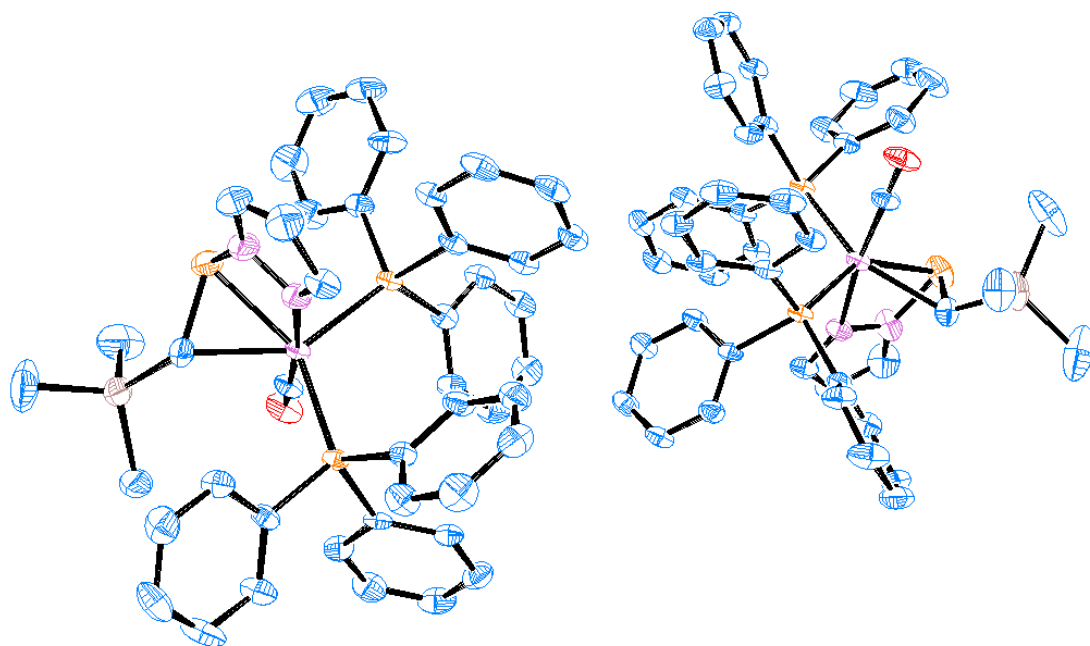


Figure 13: Structure of **5** in crystals of the DCM solvate. 50% thermal ellipsoids. H atoms and solvent molecules omitted for clarity.

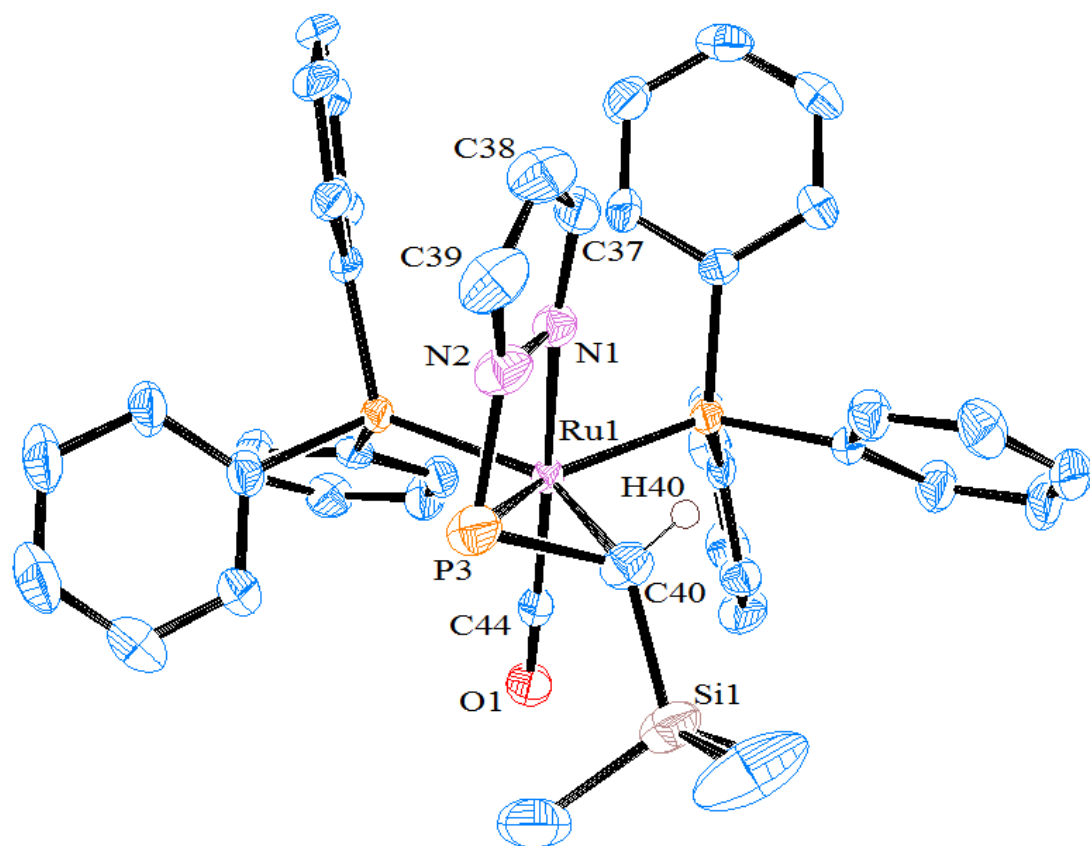
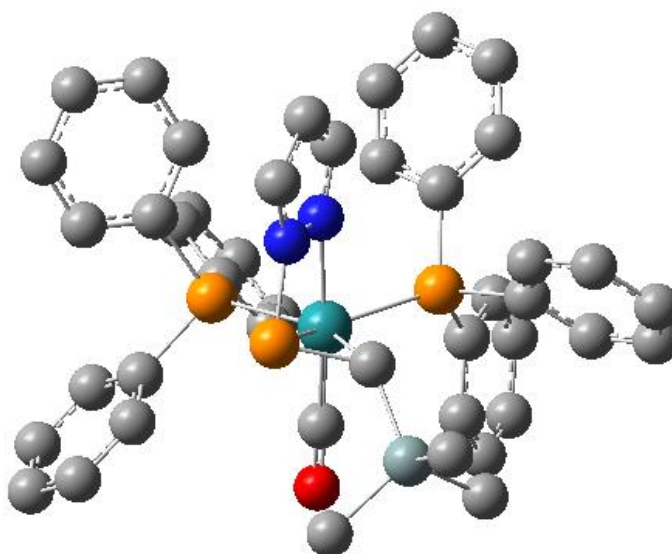


Figure 14: Molecular structure of one molecule of **5**. 50% thermal ellipsoids. H atoms omitted for clarity.

Table 2: Selected bond lengths (Å) and angles (°) for **5**.

	X-Ray	DFT
Ru(1)–C(40)	2.213(5)	2.239
Ru(1)–P(3)	2.3806(16)	2.446
Ru(1)–N(1)	2.177(4)	2.251
P(3)–C(40)	1.779(6)	1.797
P(3)–N(2)	1.809(5)	1.827
Ru(1)–C(40)–H(40)	112.4	108.52
P(3)–C(40)–H(40)	112.4	113.87
Si(1)–C(40)–H(40)	112.4	110.18

Data obtained from DFT studies of **5** (Figure 15, Table 2) correlate reasonably closely with X-ray diffraction data, with a P=C bond length of 1.797 Å and Ru–P/Ru–C bond lengths of 2.446/2.239 Å derived computationally compared to those found experimentally (1.779(6) Å P=C; 2.3806(16) Å Ru–P; 2.213(5) Å Ru–C). Again, bond angles ranging from 110.18°–118.37° are in close agreement to those obtained by X-ray diffraction studies (112.4°–117.2°).

Figure 15: Optimised structure of **5** calculated by DFT (B3LYP/6-31G**, LANL2DZ (Ru))

The nature of the Ru–P–C linkage was somewhat ambiguous despite the range of characterising data obtained. A P–C bond length of (1.793(6) Å) is intermediate between that generally observed for a P=C double bond (1.65–1.75 Å) and a P–C single bond (*ca.* 1.85 Å).^{151,201} A saturated sp^3 carbon centre is implied by $^1J_{CH}$ couplings of *ca.* 123 Hz (*cf.* $CH_4 \approx 125$ Hz),²⁰² which would suggest a P–C single bond in a phosphirane-type structure (Table 2, Figure 16).

This is somewhat supported by X-Ray diffraction data and DFT studies for **5**, which showed significant pyramidalisation about the phosphaaalkenic carbon, with bond angles about the P–C carbon centre of $\sim 112^\circ$, close to that expected for a tetrahedral carbon centre (*cf.* $\text{CH}_4 \approx 109.5^\circ$). However, a $\text{C}\equiv\text{O}$ stretching frequency of 1907 cm^{-1} was observed, lying in between that which might be expected for a Ru^{II} and Ru^0 mono-carbonyl complex.^{203–206}

The apparent contradictions in the above data may well be explained by the work of Cowley and Ionkin. While there are no published examples of a true metallaphosphirane-type structure, a small number of η^2 -coordinated metallaphosphaalkene complexes are known,²⁰⁷ with Cowley's seminal work in 1983 demonstrating the first example of such a complex.¹²³ The complex $[\text{Ni}(\text{PMe}_3)_2\{\eta^2\text{-P}(\text{C}(\text{SiMe}_3)_2)=\text{C}(\text{SiMe}_3)_2\}]$ exhibited a P–C bond length of $1.773(8)\text{ \AA}$, similar to that of **5** and again, lying between those expected for a typical P–C single and double bond. Cowley *et al.* attributed this to an η^2 -coordinated P=C bond, with back-donation of electron density from metal d-orbitals into the $\pi^*_{\text{P}=\text{C}}$ orbitals, causing a lengthening of the bond; this explanation was plausible given the low-lying π^* orbitals calculated previously for the compound $\text{HP}=\text{CH}_2$.²⁰⁸ Another such example is the complex $[\text{NiCl}(\text{PPh}_3)_3\{\eta^2\text{-(P}(\text{Mes}^*)=\text{CH}(\text{PPh}_3)\})]$,¹²⁵ which exhibits a phosphorus resonance at δ_{P} 21.6 attributed to the P=C phosphorus centre and a $^1J_{\text{CH}}$ coupling of 148.4 Hz. This spin–spin coupling is somewhat larger than that seen for **5** but is still smaller than that expected for sp^2 hybridization.²⁰² Bond angles about the P=C carbon centre of *ca.* 117° , similar to that of **5**, suggest pyramidalisation about the carbon centre. Additionally, a P=C bond length of $1.796(5)\text{ \AA}$ also demonstrates lengthening of the P=C bond due to retro-donation into the $\pi^*_{\text{P}=\text{C}}$ orbitals.

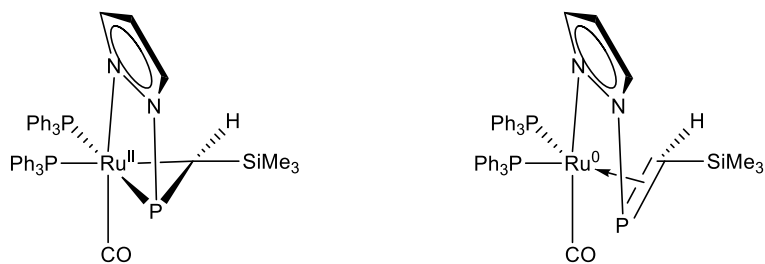


Figure 16: Two extremes of the Dewar–Chatt–Duncanson-type model, describing the nature of **5** and analogous compounds.

Literature precedent for η^2 -ruthenaphosphaalkenes is limited, with only one previously reported by Ionkin *et al.* (Figure 17).²⁰⁹ This complex exhibits similar structural features to **5**, with a P=C bond length of $1.775(3)\text{ \AA}$, significantly longer than that of the parent phosphaaalkene ($1.650(3)\text{ \AA}$). Phosphorus resonances at δ_{P} 53.8 and 31.8 were reported for this compound, with the more

deshielded resonance attributed to the P=C phosphorus centre. It is therefore reasonable to conclude that complexes **4** and **5** are better described as η^2 -coordinated phosphalkenes, with the apparent discrepancies in the structural data of **5** explained by $d \rightarrow \pi^*$ back-donation from the metal centre. As a result, the compounds lie along a structural continuum between the two extremes outlined by the Dewar–Chatt–Duncanson model (Figure 16). Back-donation not only increases the bond length from that of the parent phosphalkene but also explains the increased pyramidalisation about the P=C carbon centre.¹¹³

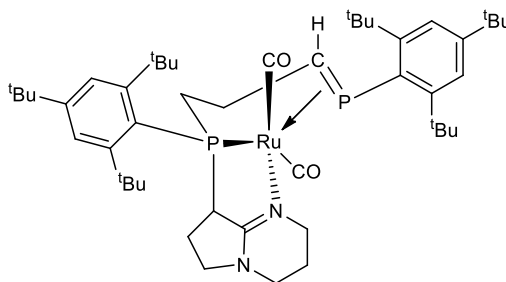
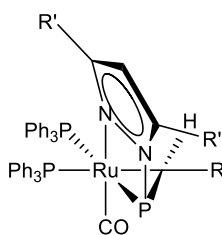


Figure 17: The previous sole example of an η^2 -ruthenaphosphaalkene.²⁰⁹

2.2.4 SYNTHESIS, STRUCTURE AND PROPERTIES OF



Complexes of the type $[\text{Ru}(\text{CO})\{\kappa^3\text{-}N,C,P\text{-}P(\text{Pz}')\text{CH}(\text{R})\}(\text{PPh}_3)_2]$ ($\text{R} = \text{SiMe}_2\text{Ph}, \text{'Bu}$) were synthesised *via* the same synthetic procedure as that for **4** and **5** (Figure 18). Complexes $[\text{Ru}(\text{CO})\{\kappa^3\text{-}N,C,P\text{-}P(\text{Pz}^*)\text{CH}(\text{SiMe}_2\text{Ph})\}(\text{PPh}_3)_2]$ (**6**) and $[\text{Ru}(\text{CO})\{\kappa^3\text{-}N,C,P\text{-}P(\text{Pz})\text{CH}(\text{SiMe}_2\text{Ph})\}(\text{PPh}_3)_2]$ (**7**) were furnished by addition of LiPz' to a solution of **3** in THF. $[\text{Ru}(\text{CO})\{\kappa^3\text{-}N,C,P\text{-}P(\text{Pz}^*)\text{CH}(\text{'Bu})\}(\text{PPh}_3)_2]$ (**8**) and $[\text{Ru}(\text{CO})\{\kappa^3\text{-}N,C,P\text{-}P(\text{Pz})\text{CH}(\text{'Bu})\}(\text{PPh}_3)_2]$ (**9**) were furnished by addition of LiPz' to a solution of **1** in THF. Each complex exhibited similar resonances in their $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, with three doublet of doublets between δ_{P} 0 and 60, with each resonance demonstrating $^2J_{\text{PP}}$ couplings between 8.2 to 50.4 Hz (Table 3).



R = SiMe₂Ph; R' = Me (**6**), H (**7**)

R = ^tBu; R' = Me (**8**), H (**9**)

Figure 18: General structure of compounds **6–9**.

Table 3: Selected ³¹P{¹H} (161.7 MHz), ¹³C{¹H} (100.5 MHz) and ¹H NMR (399.5 MHz) chemical shifts (ppm) of **4–9** in CD₂Cl₂

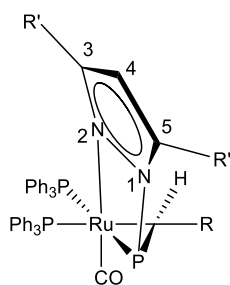
R	R'		δ_P		δ_C	δ_H
			P=C	PPh ₃	P=C	P=CH (¹ J _{CH} , Hz)
SiMe ₃	Me	4	32.9	46.6, 39.2	44.9	1.62 (123)
	H	5	58.7	46.6, 42.0	47.6	1.59
SiMe ₂ Ph	Me	6	32.3	47.0, 38.9	41.8	1.77 (128)
	H	7	57.0	47.0, 41.7	45.1	1.72 (149)
^t Bu	Me	8	14.7	45.5, 41.4	79.8	2.90 (137)
	H	9	38.8	44.2, 42.5	81.6	2.84

Notably, upon changing R' from H to Me, two of the phosphorus resonances remain almost identical. However, the third phosphorus resonance corresponding to the P=C phosphorus centre demonstrates a significant shift to lower frequency by approximately 20 ppm (Table 3). This is attributed to increased shielding of the P=C phosphorus centre due to the relative electron density of the pyrazolyl bridge. This is thought to be a result of the difference in electron donating capabilities of R'; thus, when R' = Me, there is more electron donation into the pyrazolyl ring than in the case of R' = H, resulting in a more shielded phosphorus centre. Complexes for which R = ^tBu demonstrate a P=C phosphorus resonance shifted significantly upfield compared to the silyl-analogues. For complexes **4–7**, it is likely that the available σ*-orbital associated with the silicon centre of the silyl groups reduces the electron density in the P=C bond, whereas the electron-donating effect of the ^tBu group in compounds **8** and **9** provides greater shielding of the phosphorus nucleus. Also, the ¹J_{CH} interaction observed for complex **8** (137 Hz) is more consistent with an sp² P=C carbon centre than that of its direct, silyl-based analogues (**4** = 123 Hz; **6** = 128 Hz), which is reflected in the high frequency shift of the P=CH carbon and proton resonances (δ_H = 2.90; δ_C 79.8). These data are consistent with a greater phosphalkene character of the P=C bond compared to the silyl-based derivatives.

2.3 SYNTHESIS AND PROPERTIES OF



In order to further investigate the influence that the substituents on the pyrazolyl ring have on the P=C phosphorus centre, a series of analogous complexes was synthesised. Addition of the lithium pyrazolates $\text{LiPz}^{\text{Me,CF}_3}$, $\text{LiPz}^{\text{CF}_3}$ and LiPz^{tBu} to complexes **2** and **3** yielded the target compounds **10–14** (Figure 19, Table 4).



- R = SiMe₃; R' = H; R'' = ^tBu (**10**)
 R = SiMe₃; R' = Me; R'' = CF₃ (**11**)
 R = SiMe₃; R' = H; R'' = CF₃ (**12**)
 R = SiMe₂Ph; R' = Me; R'' = CF₃ (**13**)
 R = SiMe₂Ph; R' = H; R'' = CF₃ (**14**)

Figure 19: $[\text{Ru}(\text{CO})\{\kappa^3\text{-}N,C,P\text{-P}(\text{Pz}^{\text{R/R''}})\text{CH}(\text{R})\}(\text{PPh}_3)_2]$ (**10–14**).

Interestingly, complex **10** exhibits a significantly higher frequency shift of the P=C phosphorus resonance compared to that of complexes **4–9**; it is unclear at this stage why the combined effect of H and ^tBu at the R' and R'' positions has caused extensive deshielding. The orientation of the pyrazolyl ring for compound **10** was deduced by ¹³C{¹H} NMR and ¹³C/¹H-HSQC and HMBC spectra. It might be expected that the C⁵ atom of the pyrazolate would bear the ^tBu substituent due to steric considerations. This is somewhat supported by a ¹³C{¹H} NMR spectrum: only two of the Pz carbon atoms demonstrate a *J*_{CP} coupling (δ_{C} 100.8; d, ³*J*_{CP} = 3.27 Hz; δ_{C} 157.8, d, ²*J*_{CP} = 4.01 Hz), which are assigned to the C⁴ and C⁵ positions. The protons of the ^tBu group only demonstrate an interaction with one of these resonances (δ_{C} 157.8) in a ¹³C/¹H-HMBC experiment. Therefore, it was concluded that R'', in this case the ^tBu group, is at the C⁵ position and R' (H) is in the C³ position (δ_{C} 157.8 (C⁵), 100.8 (C⁴), 140.0 (C³)).

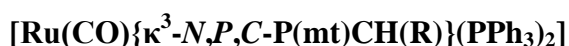
The orientation of the pyrazolate ring in complexes **11–14** were difficult to deduce due to very weak signals in the NMR spectra. A multiplet resonance in each of the ³¹P{¹H} NMR spectra for complexes **10–14** between δ_{P} 62.7 and 76.7 was assigned to the phosphaaalkenic phosphorus centres; for fluorinated complexes **11–14**, this resonance was observed as a doublet of doublet

of quartets, arising from $^2J_{\text{PP}}$ coupling to both PPh_3 ligands and a $^4J_{\text{PF}}$ coupling to the CF_3 substituent. The two resonances assigned to the PPh_3 ligands in complexes **11–14** do not show a J_{CF} coupling, suggesting that the CF_3 group is located at the C^5 position of the pyrazolate ring. It is evident that the electron-withdrawing effect of the CF_3 substituent causes greater deshielding of the $\text{P}=\text{C}$ phosphorus centre as expected. In addition, the effect of the substituents H vs. Me for complexes **11–14** shows the same pattern as previously observed for complexes **4–9** *i.e.* the methyl substituent causes greater shielding of the $\text{P}=\text{C}$ phosphorus centre than H.

Table 4: Selected $^{31}\text{P}\{^1\text{H}\}$ (161.7 MHz), $^{13}\text{C}\{^1\text{H}\}$ (100.5 MHz), ^1H NMR (399.5 MHz) and ^{19}F NMR (375.9 MHz) chemical shifts (ppm) for complexes **10–14** in CDCl_3

R	R', R''		δ_{P}		δ_{C}	δ_{H}	δ_{F}
			$\text{P}=\text{C}$	PPh_3	$\text{P}=\text{C}$	$\text{P}=\text{CH}$	CF_3
	H, ^tBu	10	66.4	46.4, 41.4	46.3	1.52	N/A
SiMe_3	Me, CF_3	11	64.6	46.9, 38.4	45.2	1.76	−60.0
	H, CF_3	12	76.6	47.7, 41.5	47.1	1.78	−60.1
SiMe_2Ph	Me, CF_3	13	62.7	47.2, 38.3	41.8	1.97	−59.8
	H, CF_3	14	74.9	48.0, 38.3	46.7	1.97	−60.1

2.4 SYNTHESIS AND PROPERTIES OF COMPLEXES OF THE TYPE



In addition to synthesis of the pyrazolyl compounds **4–14**, the reaction of lithium methimazolyl (mt) with **2** and **3** was carried out to give some insight into the effect of different donor atoms on the $\text{P}=\text{C}$ phosphorus centre. Two isomers were formed in each reaction (Figure 20); the preferential formation of one isomer over the other was of particular interest, potentially shedding light on the electronic properties of the parent phosphalkenes (Table 5). $^n\text{BuLi}$ was added to a solution of Hmt in THF under ambient conditions and the resultant lithium methimazolyl added to a solution of **2**. A mixture of the two possible coordination isomers – $[\text{Ru}(\text{CO})\{\kappa^3\text{-}N,P,C\text{-P}(N\text{-mt})\text{CH}(\text{Si}(\text{CH}_3)_3)\}(\text{PPh}_3)_2]$ (**Ru-N-15**) and $[\text{Ru}(\text{CO})\{\kappa^3\text{-}S,P,C\text{-P}(S\text{-mt})\text{CH}(\text{Si}(\text{CH}_3)_3)\}(\text{PPh}_3)_2]$ (**Ru-S-15**) – was furnished in 4:1 ratio (Figure 20, Table 5).

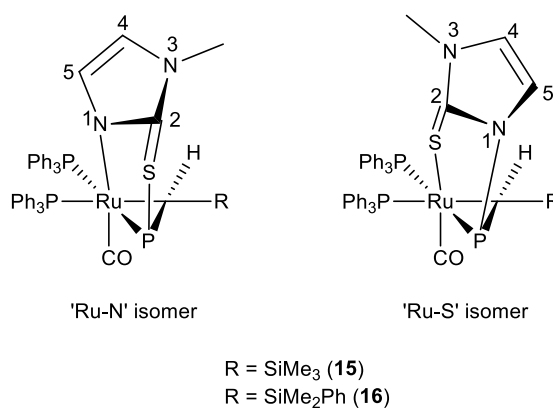


Figure 20: Two isomers synthesised upon addition of Li(mt) to **2** and **3**.

Ru-N-15 was characterised by three multiplet resonances in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at δ_{P} 44.6 (dd, $^2J_{\text{PP}} = 9.6, 5.4$ Hz), 41.7 (dd, $^2J_{\text{PP}} = 54.0, 5.4$ Hz) and 38.5 (dd, $^2J_{\text{PP}} = 54.0, 9.6$); these data are similar to those of compounds **4–14**, suggesting formation of analogous η^2 -phosphaalkene complexes. A ^1H NMR spectrum of the mixture exhibited two resonances at δ_{H} 6.09 and 5.73, assigned to the alkenic protons at the C⁴ and C⁵ positions of the methimazolyl ring, respectively. Retention of the P=CH(SiMe₃) fragment was confirmed by resonances at δ_{H} 0.90 (d, $^2J_{\text{HP}} = 6.0$ Hz) and -0.17 (s), with a relative integration of 1:9; further, a broad multiplet resonance at δ_{C} 28.0 in a $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum was observed, assigned to the P=C carbon centre on the basis of HSQC and HMBC experiments. These data are summarised in Table 5.

Similar data were observed for **Ru-S-15**, with phosphorus resonances observed at δ_{P} 85.3 (d, $^2J_{\text{PP}} = 50.0$ Hz), 44.6 (a multiplet obscured by other resonances) and 39.0 (dd, $^2J_{\text{PP}} = 50.0, 12.50$ Hz). The ^1H NMR spectrum exhibited two resonances at δ_{H} 6.62 and 6.36, assigned to the alkenic protons with the former observed as a multiplet which appeared to be overlapping doublets, suggesting coupling to its counterpart and a phosphorus centre. Retention of the P=CH(SiMe₃) fragment was again confirmed by resonances at δ_{H} 1.09 and -0.17 , with a relative integration of 1:9. A broad multiplet resonance at δ_{C} 25.1 in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum was observed and assigned to the P=C carbon centre by HSQC and HMBC experiments. Bulk purity of the isomeric mixture was confirmed by elemental analysis.

Although non-trivial, assignment of the individual isomers was based upon the H⁵ proton resonance for each isomer. One appears as an overlapping doublet of doublets in the ^1H NMR spectrum, suggesting coupling to not only the alkenic proton, but also to the P=C phosphorus centre. Additionally, an interaction is observed between this proton resonance and only one phosphorus resonance, assigned to the P=C phosphorus centre (δ_{P} 85.3) in a $^{31}\text{P}/^1\text{H}$ HMBC experiment, suggesting that these data correspond to the Ru-S-isomer. In contrast to this, the H⁵

resonance for the Ru-*N*-isomer is a very broad singlet, consistent with interactions to multiple phosphorus resonances due to its equidistant position from each phosphorus centre. This is supported by interactions observed between this proton resonance and the two PPh₃ phosphorus resonances in a ³¹P/¹H HMBC experiment.

Upon addition of lithium methimazolyl to **3**, both isomers were again synthesised, **Ru-N-16** and **Ru-S-16**, with very similar data observed; these data are also summarised in Table 5. Noteworthy features of the four compounds include the highly deshielded P=C phosphorus resonance in the ‘Ru-S’ isomer, but not the ‘Ru-N’ isomer for both **15** and **16**. A possible explanation for this is derived from the relative electronegativity of N and S, with sulfur being less electronegative than nitrogen. As a result, less electron density would be drawn away from the metal centre in the ‘Ru-S’ isomer than the ‘Ru-N’ isomer, allowing a greater degree of back donation into the P=C π*-orbitals from the metal d-orbitals; this would cause a lengthening of the P=C bond rendering the Ru–P–C linkage more phosphirane-like in nature (*vide supra*, Figure 16).²¹⁰ The deshielding of phosphorus might also be enhanced by the more electronegative nitrogen atom bound to it in the ‘Ru-S’ isomer, which would draw electron density away from the phosphorus centre more so than sulfur in the ‘Ru-N’ isomer.

Another seemingly spurious aspect of the data is the multiplet nature of the P=CH proton resonance of the ‘Ru-S’ isomer in the ¹H NMR spectrum. Whilst the ‘Ru-N’ isomer for both **15** and **16** exhibits a doublet coupling for this resonance, arising from a ²J_{HP} interaction, the ‘Ru-S’ isomer presents a more complex multiplet – seemingly a doublet of doublets. As the ‘Ru-S’ isomer appears to be more phosphirane-like in nature than the ‘Ru-N’ isomer, the Ru–C bond would likely be stronger, perhaps facilitating a ³J_{HP} interaction with the PPh₃ phosphorus centres. It would be conceivable in this case that the proton could present a ³J_{HP} interaction with the PPh₃ ligands, with one coupling much larger than the other due to the pseudo *trans*- position of the CH fragment with one of the PPh₃ units.

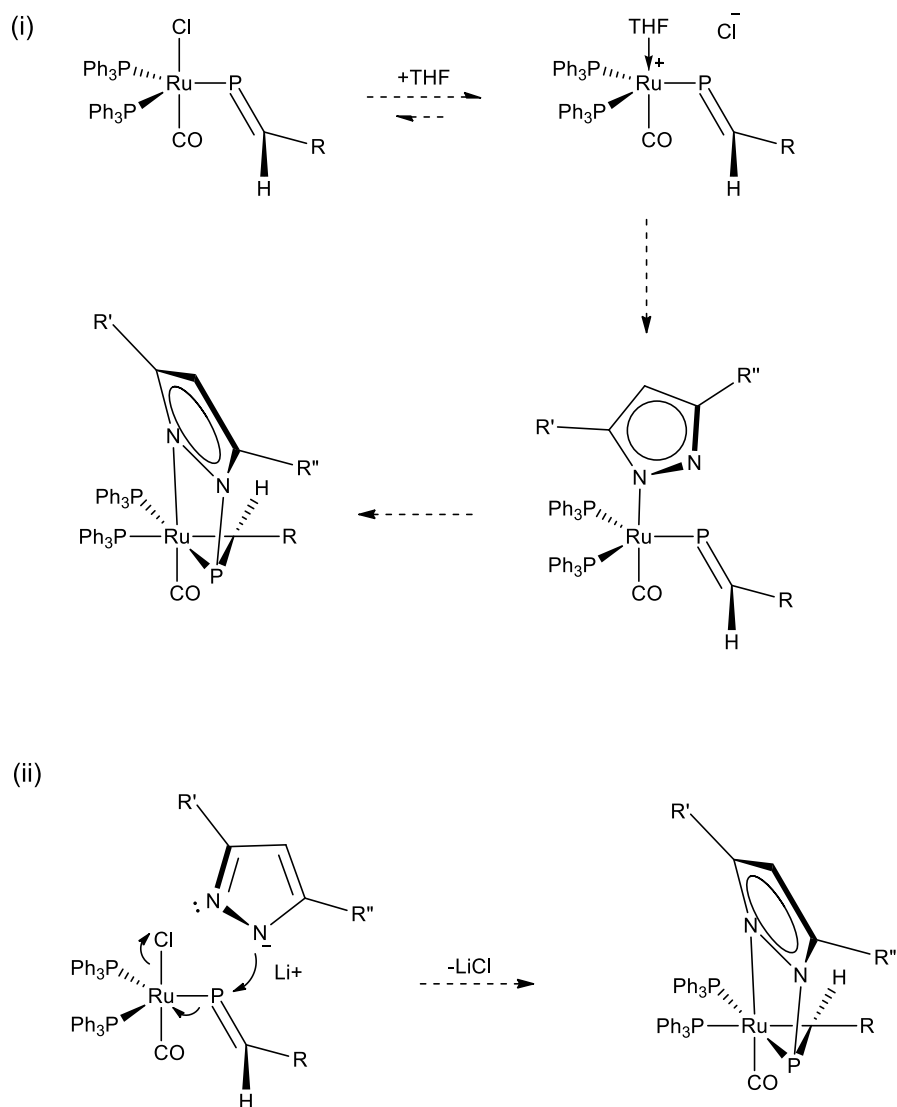
Table 5: Selected $^{31}\text{P}\{^1\text{H}\}$ (161.7 MHz) and ^1H NMR (399.5 MHz) (ppm) and spin-spin couplings (Hz) for both isomers of compounds **15** and **16** in CD_2Cl_2

R	Nucleus	‘Ru- <i>N</i> ’ isomer	‘Ru- <i>S</i> ’ isomer	Assignment
15 SiMe ₃	$^{31}\text{P}\{^1\text{H}\}$	dd, 41.72 (54.0, 5.4)	d, 85.3 (50.0)	$P=\text{C}$
		dd, 44.6 (9.6, 5.4)	44.6 (m)	$P\text{Ph}_3$
		dd, 38.5 (54.0, 9.6)	dd, 39.0 (50.0, 12.5)	$P\text{Ph}_3$
	^1H	d, 6.09 (1.7)	d, 6.36 (2.2)	H^4
		s, 5.73 (br)	m, 6.62	H^5
		d, 0.90 (6.0)	m, 1.09	$P=\text{CH}$
16 SiMe ₂ Ph	$^{31}\text{P}\{^1\text{H}\}$	dd, 44.0 (54.6, 5.2)	d, 85.9 (51.6)	$P=\text{C}$
		dd, 44.4 (9.4, 5.2)	dd, 44.6 (12.0, 4.2)	$P\text{Ph}_3$
		dd, 38.2 (54.6, 9.4)	dd, 38.8 (51.6, 12.0)	$P\text{Ph}_3$
	^1H	s, 6.03 (br)	s, 6.21 (br)	H^4
		s, 5.75 (br)	s, 6.57 (br)	H^5
		d, 0.99 (6.04)	m, 1.17	$P=\text{CH}$

2.5 MECHANISTIC STUDIES

2.5.1 REACTIONS OF $[\text{RuCl}(\text{CO})(\text{PPh}_3)_2(\text{P}=\text{CHSiMe}_2\text{R})]$ (R = Me (**2**), Ph (**3**)) WITH NITROGEN- AND CARBON-BASED NUCLEOPHILES

While it is clear that a nucleophilic species has added to the parent complexes **1**, **2** and **3** in the formation of complexes **4–16**, the mechanism by which this occurred is unclear. Possible mechanisms involve: (i) coordination of THF to the metal centre facilitating loss of Cl^- , followed by coordination of the pyrazolyl ring to the metal centre and subsequent nucleophilic attack at $\text{P}=\text{C}$; (ii) nucleophilic attack by the pyrazolyl ring at the $\text{P}=\text{C}$ phosphorus, with subsequent coordination to Ru through the second nitrogen donor (Scheme 34). In order to glean insight into these processes, a series of nitrogen-based nucleophiles was initially added to **2** and **3**; the atom to which the nucleophile binds, *i.e.* ruthenium or phosphorus, gave some indication of the initial stages of the mechanism leading to complexes **4–16**.



Scheme 34: Possible mechanisms for the formation of complexes **4–16** via (i) initial coordination of the pyrazolyl ring to the ruthenium centre and (ii) initial nucleophilic attack at the phosphaaalkenic phosphorus centre.

To a solution of **2** was added $\text{LiN}(\text{SiMe}_3)_2$ in THF under ambient conditions and the mixture stirred for 1 h. A new product (complex type **A**) was observed in the crude reaction mixture. A proposed structure for complex type **A** is shown in Scheme 36 and will be considered in the following discussion. Two multiplet resonances were observed in a $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of compound **A-1** at δ_{p} 290.7 (t, $^2J_{\text{PP}} = 34.4$ Hz) and δ_{p} 18.5 (d, $^2J_{\text{PP}} = 34.4$ Hz) (Table 6). These data are consistent with retention of a $\text{P}=\text{C}$ bond with η^1 -coordination to a metal centre through the phosphorus lone pair.^{156,211,212} A $^2J_{\text{PH}}$ coupling in a proton coupled ^{31}P NMR experiment is consistent with retention of the alkenic proton and is further supported by resonances in the ^1H NMR spectrum at δ_{H} 7.72 and 0.02, assigned to the $\text{P}=\text{CH}$ and SiMe_3 protons, respectively,

suggesting retention of the P=CH(SiMe₃) fragment. The protons of the N(SiMe₃)₂ fragment are observed at δ_{H} -0.05, in stoichiometric ratio with the protons of the SiMe₃ and CH units of the phosphaaalkenic fragment; however, no interaction is observed between the amide fragment and the P=C phosphorus centre in a ³¹P/¹H-HMBC experiment. This may be due to a weak ⁴J_{PH} coupling or alternatively, the N(SiMe₃)₂ fragment is not bound to phosphorus.

Reaction of LiNⁱPr₂ and **2** gave remarkably similar results, with another complex of type **A** (**A-2**) formed. Two major, mutually coupling resonances were observed in the ³¹P{¹H} NMR spectrum at δ_{P} 290.7 (t, ²J_{PP} = 34.7 Hz) and δ_{P} 18.5 (d, ²J_{PP} = 34.7 Hz) (Table 6). Retention of the P=CH(SiMe₃) unit was supported by ¹H NMR spectroscopy, with resonances at δ_{H} 7.71 and 0.02 assigned by HSQC/HMBC experiments to the P=CH and SiMe₃ protons, respectively. The P=C carbon centre could not be observed directly in a ¹³C{¹H} NMR spectrum, but its presence was inferred by 2D experiments. The presence of excess LiNⁱPr₂ is observed in the ¹H NMR spectrum (δ_{H} 2.90, 1.05; ³J_{HH} = 6.25 Hz); while it is possible that a ⁻NiPr₂ unit associated with the resultant compound is obscured by the excess LiNⁱPr₂, no interaction is observed with any of the phosphorus resonances in a ³¹P/¹H HMBC experiment.

Interestingly, a further example of an **A**-type complex (**A-3**) was obtained from attempts to prepare [Ru(CO){ κ^3 -N,C,P-P(Pz^{(CF₃)₂)CH(SiMe₃))(PPh₃)₂] by reaction of **2** with LiPz^{(CF₃)₂}. A multiplet resonance was observed in a ³¹P NMR spectrum (δ_{P} 290.7; ²J_{PP} = 35.0 Hz, ²J_{HP} = 16.1 Hz) alongside a doublet resonance (δ_{P} 18.5, ²J_{PP} = 35.0 Hz); the J_{HP} coupling observed for the P=C phosphorus centre suggests retention of the alkenic proton, confirmed by a broad doublet in the ¹H NMR spectrum at δ_{H} 7.73 (²J_{HP} = 15.7 Hz) and assigned through a ²⁹Si/¹H-HMBC experiment. Retention of the P=CH(SiMe₃) fragment is further supported by interaction of the alkenic proton with a carbon resonance at δ_{C} 154.4 in a ¹³C/¹H-HSQC experiment, consistent with a P=C carbon centre. Additionally, the P=C phosphorus resonance shows an interaction with protons consistent with the SiMe₃ group, observed through a ³¹P/¹H-HMBC experiment. The pyrazolyl ring was observed in stoichiometric quantities with a broad singlet at δ_{H} 6.65 in the ¹H NMR spectrum, and a fluorine resonance at δ_{F} -56.2 in the ¹⁹F NMR spectrum shifted from that of the starting material (δ_{F} -61.7). IR spectroscopy shows a strong stretch at 1926 cm⁻¹, consistent with Ru^{II} carbonyl.^{203–205,213}}

Despite evidence to suggest retention of the pyrazolyl ring, a J_{PF} coupling was not observed in either the ³¹P{¹H} or ¹⁹F NMR spectra, suggesting that the pyrazolyl ring is not bound to the P=C phosphorus fragment. It is possible that the ring is coordinated to the Ru centre as a ⁵J_{PF} coupling might be difficult to resolve.^{214,215} However, it is expected that the pyrazolyl ring would have an effect on the relative chemical shifts of the phosphorus resonances if it were

bound to the molecule. It would therefore seem unlikely given the identical phosphorus chemical shifts of compounds **A-1** to **A-4**.

Table 6: Selected $^{31}\text{P}\{^1\text{H}\}$ (161.7 MHz), $^{13}\text{C}\{^1\text{H}\}$ (100.5 MHz) and ^1H NMR (399.5 MHz) chemical shifts (ppm) for complexes of type **A(1–4)** in CDCl_3

Compound ID	LiNu	δ_{P}		δ_{C}		δ_{H}
		PPh_3 ($^2J_{\text{PP}}$, Hz)	$\text{P}=\text{C}$ ($^2J_{\text{PP}}$, Hz)	$\text{P}=\text{C}$ ($^1J_{\text{CP}}$, Hz)	$\text{P}=\text{CH}$ ($^2J_{\text{HP}}$, Hz)	
A-1	$\text{LiN}(\text{SiMe}_3)_2$	18.5 (34.4)	290.7 (34.4)	154.6 (34.0)	7.72 (br)	0.02
A-2	LiN^iPr_2	18.5 (34.7)	290.7 (34.7)	154.6 (br)	7.71 (15.7)	0.02
A-3	$\text{LiPz}^{(\text{CF}_3)_2}$	18.5 (35.0)	290.7 (35.0)	154.4 (33.4)	7.73 (15.7)	0.03
A-4	$\text{LiPz}^{(\text{tBu})_2}$	18.5 (34.5)	290.7 (34.5)	154.7 (33.9)	7.72 (15.5)	0.02

The difference in reactivity between $\text{LiPz}^{(\text{CF}_3)_2}$ and other LiPz' complexes is possibly due to increased steric bulk about the pyrazolyl ring. In order to demonstrate this, reaction of **2** with the bulky pyrazolate $\text{LiPz}^{(\text{tBu})_2}$ was attempted. Reaction of the $\text{LiPz}^{(\text{tBu})_2}$ with **2** did indeed furnish a compound of type **A** (**A-4**) as anticipated, along with a second unknown species (*vide infra*). The resultant product showed a triplet resonance at δ_{P} 290.7 and 18.5 in a $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, with a mutual spin–spin coupling of 34.5 Hz. Formation of **A-3** and **A-4** upon addition of $\text{LiPz}^{(\text{CF}_3)_2}$ and $\text{LiPz}^{(\text{tBu})_2}$, rather than analogues of complexes **4–14**, suggests that the steric bulk at R'' can be sufficient to prevent both nitrogen donor sites of the pyrazolate from binding to the molecule; this is later explored in greater depth (*vide infra*).

The addition of carbon-based nucleophiles was also explored. MeLi in Et_2O was added dropwise to a solution of **2** in THF under ambient conditions. Two products were observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the crude product, one of which corresponded to another complex of type **A** (**A-5**) in addition to a new unknown species (*vide infra*). For **A-5**, two multiplet resonances were observed at δ_{P} 290.7 and 18.5 with mutual spin–spin coupling ($J_{\text{PP}} = 35.0$ Hz). Similar to complexes **A-1–A-4**, there is no evidence to suggest that the nucleophile, in this case ^-Me , is bound to the molecule, with a proton-coupled ^{31}P NMR spectrum showing coupling only to the $\text{P}=\text{CH}$ proton ($^2J_{\text{HP}} = 15.7$ Hz). The presence of ^-Me within the coordination sphere of **A-5** could not be conclusively determined through ^1H NMR spectroscopy due to the formation of **A-5** in admixture with another species. A similar product (**A-6**) was yielded upon

addition of MeLi in Et₂O to **3**, with phosphorus resonances observed at δ_P 293.7 and 18.0.

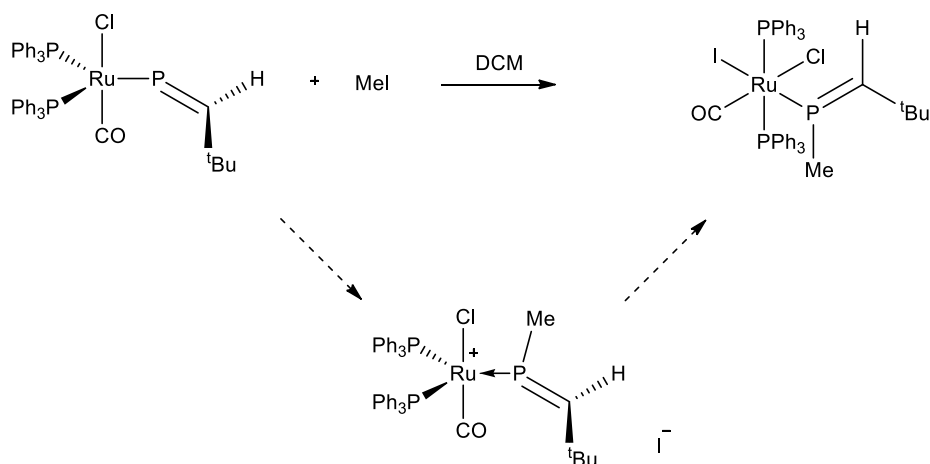
Addition of MeMgBr to **2** in THF gave rise to a very similar product (**A-7**), however, the phosphorus resonances in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shifted slightly to δ_P 287.9 and 16.6. Repeating this reaction with **3** again gave a similar product (**A-8**), with phosphorus resonances at δ_P 290.9 and 16.2. These data are summarised in Table 7; it is clear that the products formed when adding either MeLi or MeMgBr to either **2** or **3** are almost identical. It would also seem that the nature of the electrophile, *i.e.* Li⁺ or MgBr⁺, affects the relative shift in frequency of the phosphorus resonances, suggesting that it is perhaps within the coordination sphere of the metal and interacting with the complex. However, there is no evidence from 2D NMR spectra that the Me fragment is attached either to the Ru centre or the P=C phosphorus.

Table 7: Selected $^{31}\text{P}\{^1\text{H}\}$ resonances (ppm) (161.7 MHz) and $^2J_{\text{PP}}$ couplings (Hz) for compound of type **A** formed upon addition of MeLi or MeMgBr **2** or **3** in CDCl₃

Compound ID	R	E ⁺	δ_P	
			$P\text{Ph}_3$ ($^2J_{\text{PP}}$, Hz)	$P=\text{C}$ ($^2J_{\text{PP}}$, Hz)
A-5	SiMe ₃	Li	d, 18.5 (34.6)	t, 290.7 (34.6)
A-6	SiMe ₂ Ph	Li	d, 18.0 (35.0)	t, 293.7 (35.0)
A-7	SiMe ₃	MgBr	d, 16.6 (33.6)	t, 287.9 (33.6)
A-8	SiMe ₂ Ph	MgBr	d, 16.2 (34.2)	t, 290.9 (34.2)

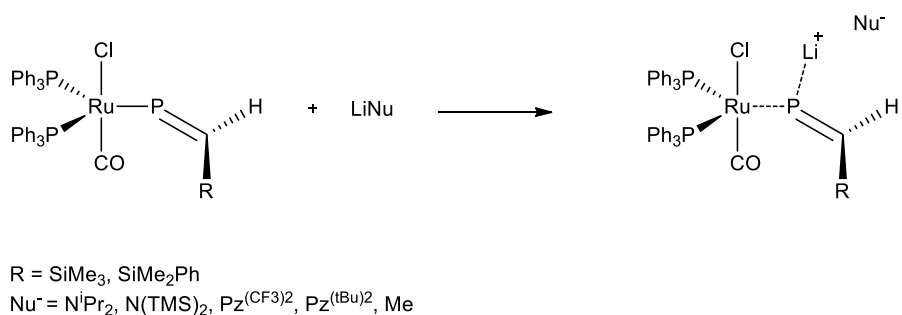
2.5.2 STRUCTURAL FEATURES OF COMPLEXES OF TYPE **A**

The dramatic shift in the P=C phosphorus resonance from the parent phosphalkenyl (*ca.* δ_P 550) in each of these examples (with both nitrogen- and carbon-based donor atoms) is consistent with a change in the bonding mode of the P=C fragment and is similar in chemical shift to that of Hill's complex $[\text{Ru}(\text{I})(\text{Cl})(\text{CO})(\text{PPh}_3)_2(\text{P}(\text{CH}_3)=\text{CH}(\text{tBu}))]$,²¹⁶ for which the P=C phosphorus resonance is observed at δ_P 225.1. This compound is formed upon addition of MeI to a solution of **1** in DCM, whereby *electrophilic* attack at the P=C phosphorus centre by Me⁺ leads to η^1 -coordination of the phosphalkene $\text{P}(\text{CH}_3)=\text{C}(\text{H})\text{tBu}$ to the metal centre through the P lone pair. The mechanism of formation of this complex is believed to proceed *via* an iodide salt intermediate, *i.e.* $[\text{RuCl}(\text{CO})(\text{PPh}_3)_2(\text{P}(\text{CH}_3)=\text{CH}(\text{tBu}))][\text{I}]$ (Scheme 35).



Scheme 35: Electrophilic attack at the P=C phosphorus centre of **1**²¹¹

The chemistry described in Scheme 35 may help to explain the products formed in the present study. It appears likely that the cation is within the coordination sphere of the metal for complexes of type **A**, as the type of cation (Li or MgBr) significantly affects the relative frequency of the phosphaaalkenic phosphorus resonance as noted from Table 7. While there is no evidence to suggest that the respective nucleophiles are directly bound to the molecule, they are consistently observed in the crude product by NMR spectroscopy. It can therefore be postulated that the nucleophilic fragment is acting as a counter-ion, akin to Hill's iodide salt, with the Li^+ cation interacting with the P=C phosphorus centre accounting for the shift in frequency in the ^{31}P NMR spectrum. Alternatively, the nucleophile may also be interacting with the Li^+ cation. A proposed structure based on the available data is shown in Scheme 36, however, the exact structure cannot be conclusively determined at this stage; analogous complexes can be postulated for the MeMgBr analogues.



Scheme 36: Reaction of **2** and **3** with LiNu yielding a complex of type **A**

2.5.3 ADDITIONAL REACTIONS OF CARBON-BASED NUCLEOPHILES



Addition of MeLi to **2** in THF under ambient conditions not only led to formation of a complex of type **A**, but also a second product (complex type **B**) in equal proportion. Upon repeating the reaction at -80°C , conversion to **B-1** alone was observed as determined by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. A series of proposed structures for complex **B** can be seen in Figure 21 and Figure 22, which will be considered in the following discussion.

Resonances for **B-1** at $\delta_{\text{P}(\alpha)}$ 33.7 (d, $J_{\text{PP}} = 27.0$ Hz), $\delta_{\text{P}(\beta)}$ 30.7 (d, $J_{\text{PP}} = 236.5$ Hz) and $\delta_{\text{P}(\gamma)}$ -4.4 (dd, $J_{\text{PP}} = 236.5, 27.0$ Hz) were observed (Table 8) and a large spin–spin coupling between P_β and P_γ is consistent with a *trans*- $^2J_{\text{PP}}$ -coupling across the Ru centre.^{217,218} Such a large ‘P–M–P’ $^2J_{\text{PP}}$ coupling has previously been demonstrated by Cole-Hamilton and co-workers with the complex $[\text{Ru}(\text{dppe})_2(\eta^2\text{-CH}_2=\text{CHPh})]$ demonstrating a *trans*- $^2J_{\text{PP}}$ -coupling of δ_{P} 293.8. For **B-1**, P_α and P_γ have a J_{PP} coupling of 27.0 Hz, consistent with a $^2J_{\text{PP}}$ interaction, however, P_α and P_β show no interaction with one another. This suggests that P_β and P_γ are directly bound to the metal centre whilst P_α is located elsewhere in the molecule.

Table 8: Selected $^{31}\text{P}\{^1\text{H}\}$ (161.7 MHz), $^{13}\text{C}\{^1\text{H}\}$ (100.5 MHz), ^1H NMR (399.5 MHz) and ^{29}Si (794 MHz) NMR chemical shifts (ppm) for compound type **B-1** upon addition of MeLi to **2**.

Nucleus	Chemical shifts, ppm (J -coupling, Hz)	Assignment
^{31}P	d, 33.7 (27.0)	$\text{P}_\alpha\text{Ph}_2$
	d, 30.7 (236.5)	$\text{P}_\beta\text{Ph}_3$
	dd, -4.4 (236.5, 27.0)	$\text{P}_\gamma\text{-CH}$
^1H	dd, 1.45 (12.6, 3.5)	P-CH_3
	dd, 1.08 (11.7, 3.2)	Ru-CH_3
	dd, 0.35 (9.4, 6.4)	P-CH
	s, -0.22	$\text{Si}(\text{CH}_3)_3$
^{13}C	m, 9.8 (br)	Ru-CH_3
	m, 6.5 (br)	P-CH_3
	m, 2.2 (br)	$\text{Si}(\text{CH}_3)_3$
	-1.3 (br)	P-CH
^{29}Si	s, 4.1	$\text{Si}(\text{CH}_3)_3$

The CH(SiMe₃) fragment appears to have been retained, with ¹H NMR spectroscopy revealing a singlet resonance at δ_{H} -0.22 integrating in a 9:1 ratio with respect to a doublet of doublets at δ_{H} 0.35 (J_{HP} = 6.4, 9.4 Hz). Both resonances correlate with a silicon resonance at δ_{Si} 4.1 and a broad carbon resonance at δ_{C} -1.3, observed through ²⁹Si/¹H- and ¹³C/¹H-HMBC experiments, respectively. The relative frequency of this carbon centre has, however, shifted to a significantly lower frequency compared to that of **2**, perhaps suggesting that the P=C bond has been reduced to a P-C single bond. The CH proton resonance shows a strong interaction with P_α and P_γ, whereas no interaction is observed with P_β. This, in combination with the large J_{PP} coupling between P_β and P_γ, is consistent with P_β corresponding to a PPh₃ ligand located *trans*- to P_γ, with the latter assigned to the P-CH phosphorus resonance. P_α appears to be a PPh_n ligand, with the phosphorus resonance showing strong interactions with aryl groups in the ¹H NMR spectrum. Given that this ligand is not bound to the metal centre and its coupling to P_γ is inconsistent with a ¹ J_{PP} interaction, it is suggested that this ligand may be bound to the P-CH carbon centre. Two doublet of doublet resonances are observed in the ¹H NMR spectrum at δ_{H} 1.45 (J_{PP} = 12.6, 3.5 Hz) and δ_{H} 1.08 (J_{PP} = 11.7, 3.2 Hz), both integrating to 3 protons, presumably corresponding to CH₃ groups. Both resonances show an interaction with P_β and P_γ, but show J_{HP} couplings of differing magnitudes (Table 8). Of the two methyl groups, only the more deshielded resonance shows an interaction with the SiMe₃ protons. It might therefore be concluded that this methyl group is bound to P_γ, with the other located at the metal centre. The relative position of the three phosphorus centres and two methyl groups is represented in Figure 21 and Figure 22.

Infrared spectroscopy demonstrates retention of a C≡O ligand, with a stretching frequency of 1920 cm⁻¹ indicating a Ru centre in the +2 oxidation state (*vide supra*). It is possible that the chloride ligand may have been retained. On this basis, a proposed structure is shown in Figure 21, whereby P_α is assigned to a phosphonium ion with a formal negative charge on Ru. Mass spectrometry reveals a peak at m/z 801 attributable to [M⁺ - Cl], in addition to a peak at m/z 380, attributable to the [P_γ-CH(P_αPh₃)(SiMe₃)]⁺ fragment. This structure does not, however, account for the fate of the two equivalents of Li⁺.

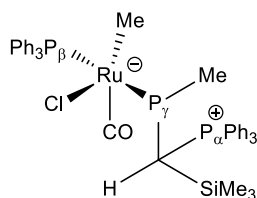


Figure 21: Proposed structure of complex type **B**, formed upon addition of MeLi or MeMgBr to complex **2**.

Analogous complexes were observed upon addition of MeMgBr to **2** (**B-2**) and upon addition of either MeLi or MeMgBr to **3** (**B-3** and **B-4**, respectively) (Table 9). Little difference is observed in the NMR data between these analogues, however, upon addition of MeMgBr a more significant shift upfield is observed for P_γ compared to MeLi, illustrating a greater degree of shielding; this is also observed in complexes of type **A**. This perhaps suggests that both Li^+ and BrMg^+ are interacting with this phosphorus centre to some degree, which is not accounted for in the proposed structure depicted in Figure 21. Positive ion mass spectrometric data is seemingly consistent with this hypothesis: for Li containing products, mass numbers of the expected fragments are frequently found to be too large by approximately 7, while MgBr containing compounds demonstrate mass numbers larger than that expected by approximately 104 (MgBr). However, this raises questions as to the overall charge of the molecule and the fate of the second equivalent of $\text{Li}^+/\text{BrMg}^+$.

Table 9: Selected $^{31}\text{P}\{^1\text{H}\}$ (161.7 MHz) and ^1H NMR (399.5 MHz) data for compounds **B-1–B-4** upon addition of MeLi or MeMgBr to **2** and **3** in CDCl_3

		Multiplicity, Chemical Shift in ppm (Coupling in Hz)		Assignment
		R = TMS	R = SiMe_2Ph	
MeLi	^{31}P	d, 33.7 (27.0)	d, 33.6 (27.3)	$P_\alpha\text{Ph}_2$
		d, 30.7 (236.5)	d, 30.9 (236.0)	$P_\beta\text{Ph}_3$
		dd, -4.4 (236.47, 27.0)	dd, -2.9 (236.0, 27.3)	$P_\gamma\text{-CH}$
	^1H	dd, 1.45 (12.56, 3.5)	dd, 1.34 (12.4, 2.6)	P-CH_3
		dd, 1.08 (11.74, 3.2)	dd, 0.73 (12.1, 2.9)	Ru-CH_3
		dd, 0.35 (9.42, 6.4)	dd, 0.96 (m, br)	P-CH
		s, -0.22	s, 0.29, 0.16	$\text{Si(CH}_3\text{)}$
MeMgBr	^{31}P	d, 32.1 (27.2)	d, 31.0 (27.0)	$P_\alpha\text{Ph}_2$
		d, 29.6 (234.4)	d, 29.0 (234.6)	$P_\beta\text{Ph}_3$
		dd, -8.1 (234.4, 27.2)	dd, -7.0 (234.58, 27.0)	$P_\gamma\text{-CH}$
	^1H	dd, 1.60 (12.4, 3.4)	dd, 1.42 (11.9, 2.6)	P-CH_3
		dd, 1.04 (11.8, 3.2)	0.67 (11.9, 2.6)	Ru-CH_3
		dd, 0.35 (9.1, 6.2)	0.90 (m, br)	P-CH
		s, -0.18	s, 0.10, -0.28	$\text{Si(CH}_3\text{)}$

Notably, an excess of THF was observed in the crude ^1H NMR spectra for all complexes of type **B**. While it is not possible to distinguish bound from free THF in the obtained spectra, it may support the notion that THF is coordinating to the metal centre with loss of MCl , thereby satisfying the coordination number of Ru. A proposed structure based on these assumptions is shown in Figure 22, (a).

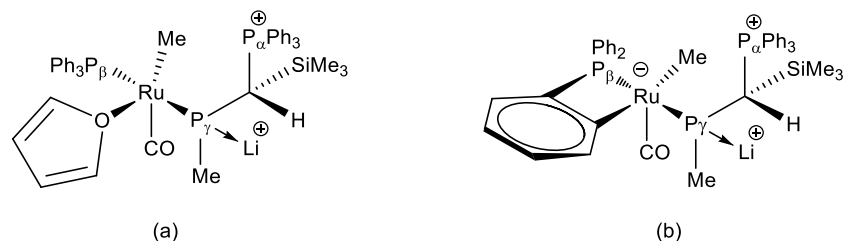


Figure 22: Proposed structures of complex type **B** given loss of Cl^- facilitated by (a) coordination of THF and (b) orthometallation.

An alternative product could be that of species (b) (Figure 22), arising from orthometallation of the PPh_3 ligand, facilitated by the presence of an alkyl lithium reagent in excess, with subsequent loss of MeH . Loss of LiCl upon addition of Me^- to the metal centre would then be conceivable as the orthometallation step would account for the coordination number of Ru. It might be expected that a carbon-proton through-bond interaction would be observed in an HMBC NMR experiment between the CH_3 protons of the Ru-Me group and the Ru-C carbon centre of the orthometallated ring – such an interaction is not, however, observed. In addition, this proposed structure again raises questions as to the overall charge of the molecule and the fate of the hydride. However, with the available data, it is not possible at this stage to determine conclusively the nature of complex type **B**.

2.5.4 REACTIONS OF HPz^* WITH COMPLEXES $[\text{RuCl}(\text{CO})(\text{PPh}_3)_2(\text{P}=\text{CHR})]$ ($\text{R} = ^t\text{Bu}$ (**1**), SiMe_3 (**2**), SiMe_2Ph (**3**))

To further explore the mechanism of formation of complexes **7–21**, the free pyrazole HPz^* was reacted with complexes **1–3**. The reactions with free pyrazole were explored in order to assess the likelihood of preferential coordination to the metal, as opposed to attack at the phosphorus centre, when there is only one available donor atom. HPz^* and **1** were dissolved in THF and stirred under ambient conditions for 1 h. Two major products, labelled complex types **C** and **D** (**C-1** and **D-1**, respectively) and free PPh_3 ($\delta_{\text{P}} -5.1$) were observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR

spectrum (Table 10). A proposed structure for complexes **C-1** can be seen in Figure 23.

Compound **C-1** exhibits two doublet resonances at δ_P 140.0 and 46.1 with a mutual coupling ($J_{PP} = 7.8$ Hz), the former seemingly too shielded to be a phosphaaalkenyl (*vide supra*) but too far downfield for an η^2 -phosphaalkene; the two phosphorus signals integrate 1:1, therefore it would appear that a PPh_3 group has been displaced. A $^{31}P/^1H$ HMBC experiment showed interaction between both phosphorus resonances and the proton resonances of a Pz^* ring at δ_H 5.65, 2.26 and 1.34, assigned to the CH and 2 x CH_3 groups, respectively (Table 10). It can be assumed therefore, that the pyrazolyl ring is bound to the Ru centre. The NH proton of this pyrazolyl group was not observed spectroscopically.

Table 10: Selected $^{31}P\{^1H\}$ (161.7 MHz), $^{13}C\{^1H\}$ (100.5 MHz) and 1H NMR (399.5 MHz) NMR chemical shifts (ppm) and spin–spin couplings (Hz) for compounds **C-1** and **D-1**, formed upon reaction of HPz^* with **1** in $CDCl_3$

C-1	$^{31}P\{^1H\}$:	d, 140.0 (7.8)	$P-CH_2$
		d, 46.1 (7.8)	PPh_3
	1H :	2.39 (15.1)	$P-CH_2$
		1.90 (br)	$P-CH_2$
		s, 2.26, 1.34	Pz^*-CH_3
		s, 5.65 (br)	Pz^*-H^4
	$^{13}C\{^1H\}$:	d, 47.8 (46.6)	$P-CH_2$
		d, 30.7 (8.4)	$C(CH_3)_3$
		s, 11.5, 10.94	Pz^*-CH_3
		s, 149.8, 146.8	Pz^*-C
		s, 106.5	Pz^*-C^4
D-1	$^{31}P\{^1H\}$:	m, 44.2 (br)	PPh_3
	1H :	s, 11.51	Pz^*-NH
		s, 1.75, 1.58	Pz^*-CH_3
		s, 5.26	Pz^*-H^4
	$^{13}C\{^1H\}$:	s, 11.1, 10.9	Pz^*-CH_3
		s, 150.0, 139.1	Pz^*-C
		s, 106.5	Pz^*-C^4

Two multiplet resonances were observed in the 1H NMR spectrum, both integrating to 1, at δ_H 2.39 (d, $J_{HP} = 15.1$ Hz) and 1.90 (m (br)), with the latter partially obscured by other proton

environments. Interestingly, both of these proton environments show a strong interaction with one carbon resonance in a $^{13}\text{C}/^1\text{H}$ -HSQC experiment (δ_{C} 47.8; d, $^1J_{\text{CP}} = 46.6$ Hz), suggesting a CH_2 unit with magnetically inequivalent protons; this carbon resonance shows an interaction with the ^tBu unit in an $^{13}\text{C}/^1\text{H}$ -HMBC experiment. It would appear therefore, that the phosphaaalkenyl has been reduced to a $\text{P}-\text{CH}_2$ alkyl fragment; given the absence of the NH proton, N-H addition across the $\text{P}=\text{C}$ bond would provide a feasible source of H for the formation of this fragment, suggesting that the pyrazolate is also bound to the $\text{P}=\text{C}$ centre (Figure 23).

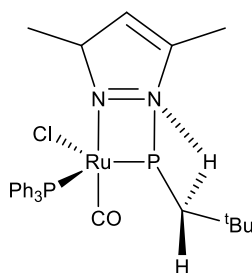


Figure 23: Proposed structure for complex type **C**, formed upon reaction of **1** with HPz^*

The proposed structure would be consistent with the dramatic low frequency shift of both the phosphorus and carbon resonances from the parent phosphaaalkene. The difference in the relative shift of the two CH_2 proton environments might be explained by intramolecular interactions between the pyrazolyl nitrogen and one of the protons, preventing rotation about the $\text{P}-\text{C}$ bond and therefore rendering the two proton environments inequivalent. While, the nature of these complexes is still somewhat ambiguous and the precise structure cannot be conclusively determined, addition of N-H across the $\text{P}=\text{C}$ bond seems plausible. Organometallic complexes incorporating $\text{P}=\text{C}$ bonds, generally in the form of pincer ligands, have been used often as catalysts for olefin hydroamination,³³ however, this would constitute the first example of hydroamination of a phosphaaalkene itself.

The unidentified species **D-1** was also observed in the crude reaction mixture, characterised by a single phosphorus resonance with second order multiplicity at δ_{P} 44.2, showing an interaction with a second pyrazole ring in a $^{31}\text{P}/^1\text{H}$ HMBC experiment. Proton resonances at δ_{H} 11.51, 5.26, 1.75 and 1.58 were observed in the ^1H NMR spectrum and assigned to the NH, CH and 2 x CH_3 protons, respectively. Almost identical phosphorus and proton shifts were observed upon addition of HPz^* to **2** (**C-2/D-2**) and **3** (**C-3/D-3**), with the latter two reactions furnishing compounds of type **D** in far greater yield than type **C**. There is no evidence to suggest that the $\text{P}=\text{CHR}$ unit has remained intact or bound to the metal centre in compounds of type **D**. Given

the second order pattern observed for the phosphorus resonance, it might be supposed that there are multiple PPh_3 units, which are all in the same environment but magnetically inequivalent. The $\text{C}\equiv\text{O}$ carbon centres cannot be seen in a $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, although this is not uncommon for transition metal carbonyls. Attempts to obtain crystals of either complex **C** or **D** have, to date, been unsuccessful. Without further data, the nature of **C** and **D** cannot be convincingly determined.

Reaction of **2** with $\text{HPz}^{(\text{CF}_3)_2}$ furnished a compound of slightly different structure to those of the type **C** compounds, which has been labelled compound **E**. A proposed structure is shown in Figure 24. $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy of the crude product exhibits a multiplet resonance at δ_{P} 254.6, far more deshielded than that observed for compound type **C**, which may reflect the electron withdrawing effect of the CF_3 groups. Two additional phosphorus resonances at δ_{P} 31.8 (d, $J_{\text{PP}} = 32.1$ Hz) and δ_{P} 31.6 (d, $J_{\text{PP}} = 18.1$ Hz) are observed, consistent with retention of both PPh_3 ligands. It is unclear at this stage why these two phosphorus centres do not appear to couple to one another. No free PPh_3 is observed in the ^{31}P NMR spectrum and compound type **D**, usually observed at δ_{P} 44.2, is also absent.

The presence of one pyrazolyl ring is inferred from ^1H NMR spectroscopy, with the pyrazolyl CH resonance observed as a broad singlet at δ_{H} 6.05. The CH_3 protons of the SiMe_3 group are also observed (δ_{H} -0.50) and show an interaction with the two CH_2 protons of the proposed $\text{P}-\text{CH}_2\text{R}$ fragment in an HMBC experiment, at δ_{H} 2.29 (dd, $J = 13.6$; $J = 7.1$ Hz) and δ_{H} 0.47 (m (br)), which appear to be inequivalent, as observed for **C**.

Two major resonances are observed in the ^{19}F NMR spectrum – a singlet at δ_{F} -62.17 and a doublet resonance at δ_{F} 57.9 ($^4J_{\text{FP}} = 41.4$ Hz). The spin-spin coupling appears to be a result of interaction with the $\text{P}-\text{CH}_2$ phosphorus centre, as it is the only multiplet phosphorus resonance, although exact couplings cannot be measured. Infrared spectroscopy shows retention of the $\text{C}\equiv\text{O}$ ligand, with a stretching frequency of 1930 cm^{-1} , suggesting a Ru^{II} centre. This is consistent with retention of the Cl^- ligand and therefore, coordination of the pyrazolate to the metal centre would seem unlikely.

Interestingly, reaction of **2** with the bulky pyrazole $\text{HPz}^{(\text{tBu})_2}$ and $^n\text{BuLi}$ furnished compounds of both type **A** as expected (*vide supra*) and of type **C**, the latter presumably arising due to the presence of $\text{HPz}^{(\text{tBu})_2}$, which had not deprotonated successfully. Phosphorus resonances were observed at δ_{P} 174.5 (d, $J_{\text{PP}} = 6.7$ Hz) and 50.6 (d, $J_{\text{PP}} = 6.7$ Hz) and integrated 1:1. Thus, it can be concluded that the preferential formation of **E** in the case of $\text{HPz}^{(\text{CF}_3)_2}$ is a result of electronic rather than steric effects. Retention of both PPh_3 ligands and the lack of coordination of the

pyrazolate to the Ru centre might be attributed to the CF_3 groups drawing electron density from the P centre, consistent with the more deshielded $\text{P}=\text{C}$ centre. This would cause there to be less electron density at the metal, which may reduce the lability of the PPh_3 ligands. Alternatively, the electron-withdrawing CF_3 groups may have reduced the electron-donating power of the nitrogen lone pair, hence preventing coordination to the Ru centre.

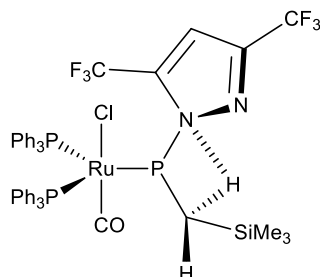
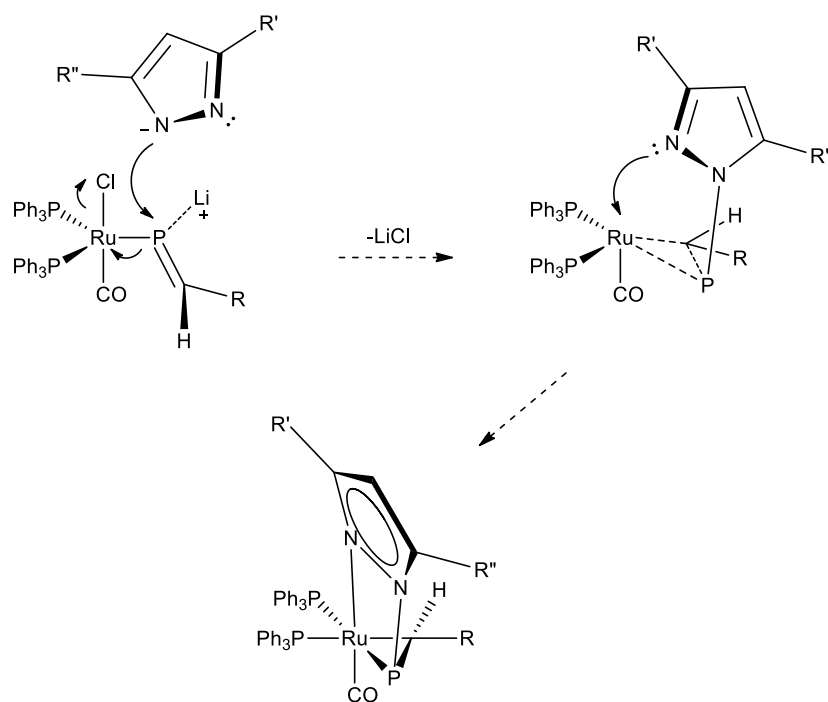


Figure 24: Proposed structure of complex type **E**, formed upon addition of $\text{HPz}^{(\text{CF}_3)_2}$ to **2**.

2.5.5 SUMMARY OF MECHANISITIC STUDIES AND THEIR IMPLICATIONS

It is possible from the mechanistic studies described to draw some conclusions regarding the mechanism of formation of complexes **4–16**. Reactions with lithiated, one-donor nucleophiles furnish complexes of type **A**, with MeLi and MeMgBr also yielding compounds of type **B**. Complexes of type **A** and **B** both seem to incorporate $^+\text{Li}/^+\text{MgBr}$, which interact with the $\text{P}=\text{C}$ phosphorus centre. It could therefore be surmised that interaction between $^+\text{Li}/^+\text{MgBr}$ and the $\text{P}=\text{C}$ phosphorus centre is the first step of the mechanism, thereby increasing the electrophilicity of phosphorus and facilitating nucleophilic attack; presumably coordination of the second nitrogen donor atom to the ruthenium centre is a result of the chelate effect. DFT studies of the parent phosphalkene **2** demonstrate a LUMO that is heavily associated with the $\text{C}=\text{P}$ bond, further supporting the notion that addition of a nucleophile will be directed to the $\text{C}=\text{P}$ bond rather than the metal centre. Indeed, the proposed structure compound **E** is in agreement with this hypothesis, with $\text{N}-\text{H}$ addition across the $\text{P}=\text{C}$ bond seemingly observed, without ligation of the second nitrogen donor atom to the metal centre, as observed for compound type **C**. While many of the reactions described do not occur without the presence of THF, it could be surmised that it is facilitating the loss of Cl^- by coordinating to the metal centre. It would seem unlikely, however, that this is the first stage of the mechanism given that complexes **C** and **E** appear to have retained their Cl^- ligands (Scheme 37).



Scheme 37: Scheme showing the possible mechanism for the synthesis of compounds **4–16** based on mechanistic studies.

2.6 CONCLUDING REMARKS

The phosphalkyne complexes $\text{P}\equiv\text{CSiMe}_2\text{R}$ were synthesised by modified literature procedures and their subsequent reaction with $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ yielded complexes **2** and **3**. DFT studies of complex **2** demonstrate a HOMO and LUMO associated with the ruthenium centre and $\text{P}=\text{C}$ bond, respectively, alongside a partial negative charge associated with the phosphorus centre, providing some explanation for the ambiphilic activity observed for this compound.

Addition of lithium pyrazolates to complexes **1**, **2** and **3** furnished a series of complexes of the type $[\text{Ru}(\text{CO})\{\kappa^3\text{-}N,C,P\text{-P}(\text{Pz}')\text{CH}(\text{R})\}(\text{PPh}_3)_2]$ ($\text{Pz}' = \text{Pz}, \text{Pz}^*, \text{Pz}^{\text{tBu}}, \text{Pz}^{\text{CF}_3}, \text{Pz}^{\text{Me,CF}_3}$; $\text{R} = \text{tBu}, \text{SiMe}_3, \text{SiMe}_2\text{Ph}$). In addition, the analogous methimazolyl complexes were synthesised from **2** and **3**, with two isomers observed for each. The pyrazolyl substituents at the C^3 and C^5 positions were shown to have a significant effect on the relative chemical shifts of the $\text{P}=\text{C}$ phosphorus centre, with the SiMe_2R and tBu groups of the phosphalkene fragment significantly affecting the nature of the Ru-P-C linkage, which lies between the two extremes of the Dewar-Chatt-Duncanson-model.

Studies to determine the mechanism by which compounds **4–16** were synthesised involved addition of single-donor nitrogen and carbon nucleophiles to compounds **2** and **3**. The apparent interaction of metal cations ($^+\text{Li}/^+\text{MgBr}$) with the P=C phosphorus centre in compounds of type **A** and **B** suggests that this may be the first stage of the mechanism, facilitating further attack at the phosphorus centre by a nucleophilic species. Addition of pyrazoles (HPz') to compound **2** led to the formation of compound types **C** and **D**, with compound **C** demonstrating, for the first time, addition of N–H across the P=C bond of a metallaphosphaalkene. Addition of $\text{HPz}^{(\text{CF}_3)_2}$ led to a similar complex (**E**), supporting the notion of nucleophilic attack at the P=C phosphorus centre due to the apparent lack of coordination of the pyrazole to the ruthenium centre. While the nature of complexes **A–E** could not be determined conclusively, aspects of their structure inferred from experimental data support the notion that addition of a nucleophile to compounds **2** and **3** will be directed to the P=C phosphorus centre, providing some insight into the formation of complexes **4–16**.

CHAPTER 3: TRANSITION METAL VINYLIDENE, ALKYNYL AND PROPARGYLIDYNE COMPLEXES AS POTENTIAL ALKYNYL-PHOSPHAALKYNE PRECURSORS

3.1 INTRODUCTION

3.1.1 ORGANOMETALLIC POLYACETYLIDES

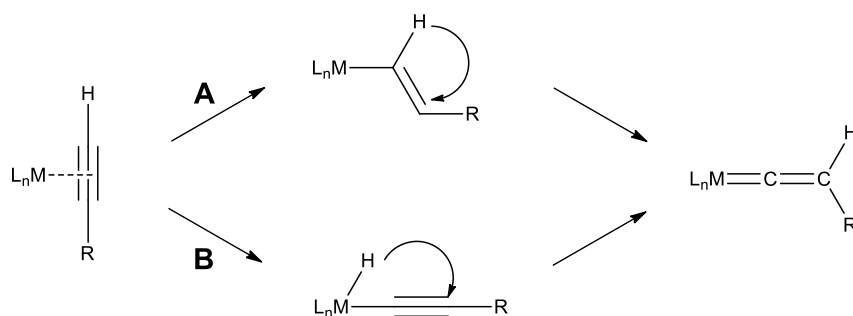
Complexes incorporating two metal centres bridged by a polyacetylenic chain have been studied extensively for application as molecular wires, due to the potential for electron transfer processes to occur through their extended π -systems. Investigation into their redox properties and electronic structure is an on-going effort by researchers in the field, with a plethora of such complexes having been demonstrated.^{219–223} Interest in such complexes stems from a variety of factors including the structural rigidity imposed by $(-C\equiv C-)_n$ chains and the variety of compounds that can be accessed, including those with σ -alkynyl ($M-C\equiv C$) or carbyne-like ($M\equiv C-C$) bonding to the metal centre. Additionally, with numerous metal–ligand configurations available as end groups for the acetylenic chains, including mono-nuclear, di-nuclear and cluster compounds, the electronic properties of these complexes can be finely tuned.^{224,225} Much of the chemistry of homo-dinuclear σ -alkynyl complexes ($M-C\equiv C-M$) has focused on the group 8 and 10 metals of the periodic table, with some of the most commonly used systems being “ $CpM(dppe)_2$ ” ($M = Fe, Ru, Os$) and “ $M'(PR_3)_2X$ ” ($M' = Pd, Pt; R = Me, Et; X = \text{halide}$).^{226–229} The more electron-rich metals are favourable for the synthesis of such complexes as alkynes tend to coordinate in an η^2 -fashion to more electron poor metals. The carbyne variants ($M\equiv C-C\equiv M$) have largely centred around the group 6 metals, particularly W and Mo, and are often associated with the tripodal hydrotripyrzolyborate ligands Tp and Tp*.^{230–234} In addition to the polyacetylides, efforts have also focused on the analogous cyanoacetylide ligands due to the isoelectronic nature of the $-C\equiv C-C\equiv N$ moiety with the diyndiyl moiety $-C\equiv C-C\equiv C-$, which exhibit similar electron transport properties.^{235–241}

Given the unique properties of the $C\equiv P$ bond (Section 1.1.4), phosphapolyynyls – acetylenic chains terminating in the $C\equiv P$ moiety ($-C\equiv C-C\equiv P$) – may prove to have advantages over the carbon and nitrogen analogues. For instance, the HOMO–LUMO band gap of P–C multiple bonds has been shown to be intrinsically low compared to their all-carbon counterparts. Smaller HOMO–LUMO band gaps have been demonstrated to enhance electron/hole transport.^{113,138,194,242–244} However, there are currently no examples of metallaphosphapolyalkynyl compounds and this is likely due to the difficulty in accessing suitable

precursors. Two routes to achieve such complexes could be envisaged, given the pre-existing examples of phosphalkyne synthesis (Section 1.1.4): i) addition of $\text{P}(\text{SiMe}_3)_3$ or $\text{LiP}(\text{SiMe}_3)_2$ to compounds of the type $[\text{L}_n\text{M}-(\text{C}\equiv\text{C})_n-\text{COCl}]$, with attack at the carbonyl carbon centre yielding an acyl-phosphine. Subsequent rearrangement to the phosphalkene followed by addition of a base may then yield the phosphalkyne; ii) preparation of a Grignard reagent from compounds of the type $[\text{L}_n\text{M}-(\text{C}\equiv\text{C})_n-\text{CH}_2\text{X}]$, followed by addition of PCl_3 to furnish a dichloropropargylphosphine of the type $[\text{L}_n\text{M}-(\text{C}\equiv\text{C})_n-\text{CH}_2\text{PCl}_2]$; double dehydrohalogenation would theoretically furnish the desired phosphalkyne fragment (Section 1.1.4). However, precursors of the type $[\text{L}_n\text{M}-(\text{C}\equiv\text{C})_n-\text{COCl}]$ and $[\text{L}_n\text{M}-(\text{C}\equiv\text{C})_n-\text{CH}_2\text{X}]$ ^{245–247} are not readily available, particularly the former of which there are no examples to date. Complexes of this type have thus been specifically targeted herein.

3.1.2 VINYLIDENE/ALKYNE TAUTOMERISATION

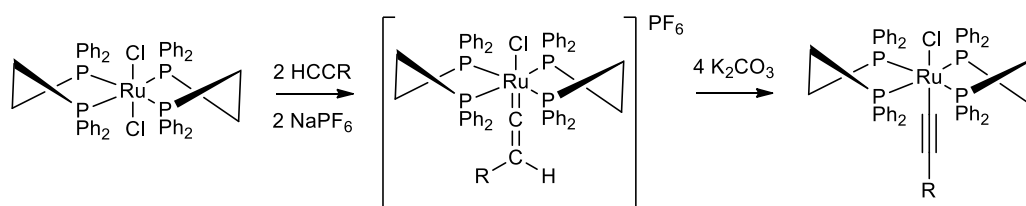
Metal–alkynyl complexes are most commonly synthesised *via* a vinylidene intermediate, with a number of well-established preparative methods having been developed. Vinylidene synthesis proceeds initially *via* η^2 -binding of the $\text{C}\equiv\text{C}$ bond of a terminal alkyne to the metal centre at a vacant coordination site. Subsequent rearrangement from the η^2 -alkyne to η^1 -vinylidene can be described by one of two mechanisms, depending on the electron density about the metal centre. The first arises due to a slippage of the $\text{C}\equiv\text{C}$ bond leading to a vinyl intermediate; in many cases the intermediate will spontaneously undergo a 1,2-hydrogen migration (Pathway **A**, Scheme 38). The second mechanism initially involves oxidative addition, yielding a hydrido–alkynyl complex; in some cases, a subsequent 1,3-hydride migration will then occur to yield the vinylidene (Pathway **B**, Scheme 38).^{248,249}



Scheme 38: Schematic showing alkyne/vinylidene tautomerisation demonstrating the two potential pathways, **A** and **B**, leading to a metal-vinylidene complex.

Group 8 metals have been used extensively to study the phenomenon of vinylidene/alkyne tautomerisation. The electron rich d^6 metals tend to be favoured for the synthesis of vinylidene and η^1 -alkynyl complexes as the initial η^2 -coordination of the alkyne is unstable due to electron repulsion of the metal's filled d_π (t_{2g}) orbital with the filled π orbitals of the alkyne. Pathway **B** is generally favoured by the electron rich metals as might be expected.^{248,249} One such example is the Ru^0 complex $[Ru(CO)_2(PPh_3)_3]$, which undergoes oxidative addition of terminal alkynes *via* Pathway **B**, without subsequent rearrangement to the vinylidene. Additionally, computational studies of the half-sandwich Ru complex $[CpRu(PMe_3)_2(\eta^2-HC\equiv CH)]$ have demonstrated that hydride migration from the metal centre to the β -carbon is a high energy process, thereby inhibiting subsequent vinylidene formation.^{248,250,251} However, it has been shown that reactions of Ru^{II} complexes tend to proceed *via* pathway **A**. This has been demonstrated both experimentally and theoretically, with *ab initio* studies demonstrating that they require substantially more energy to proceed *via* pathway **B**.^{252–254}

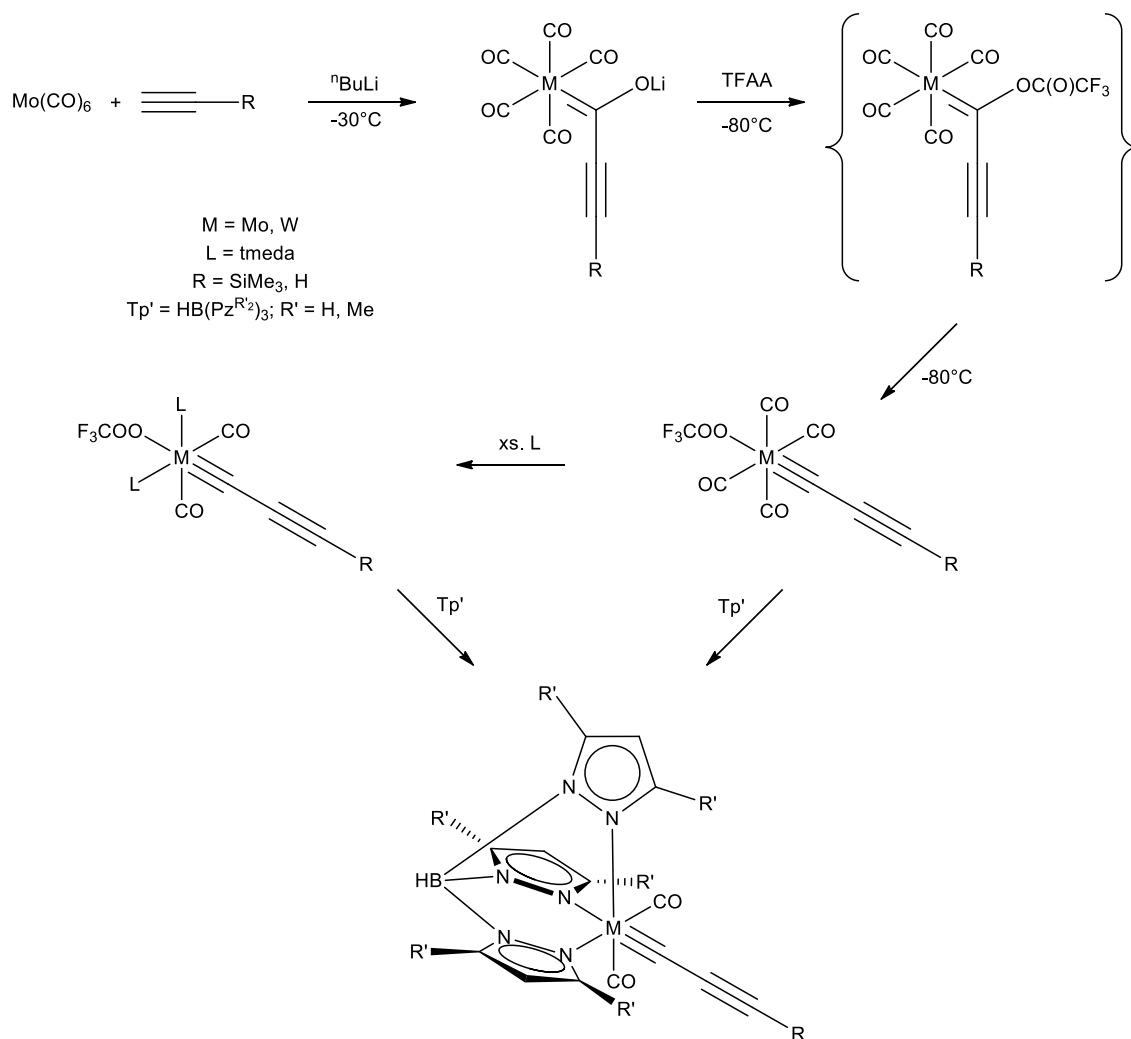
Given the need for a vacant coordination site, vinylidene/acetylide complexes are often accessed *via* abstraction of a chloride ligand from a coordinatively saturated metal complex and subsequent reaction with a terminal alkyne, with the Ru^{II} complex $[CpRuCl(PPh_3)_2]$ commonly used for such transformations.^{219,255–257} Ruthenium complexes of the type $[RuCl_2(L)_2]$ (where $L = dppe$,²⁵⁸ $dppe$ ^{259,260}) have also been used extensively for such reactions, furnishing complexes of the type $[RuCl(L)_2(C\equiv CR)]$. Addition of $NaPF_6$ or $AgOTf$ to the parent chloride complex, $[RuCl_2(L)_2]$, yields the vinylidene $[RuCl(L)_2(=C=CHR)]$, which can be isolated as the PF_6^- or OTf^- salts; alternatively, subsequent deprotonation of this intermediate furnishes the desired acetylenic product (Scheme 39).



Scheme 39: Formation of a metal-alkynyl *via* a stable vinylidene intermediate

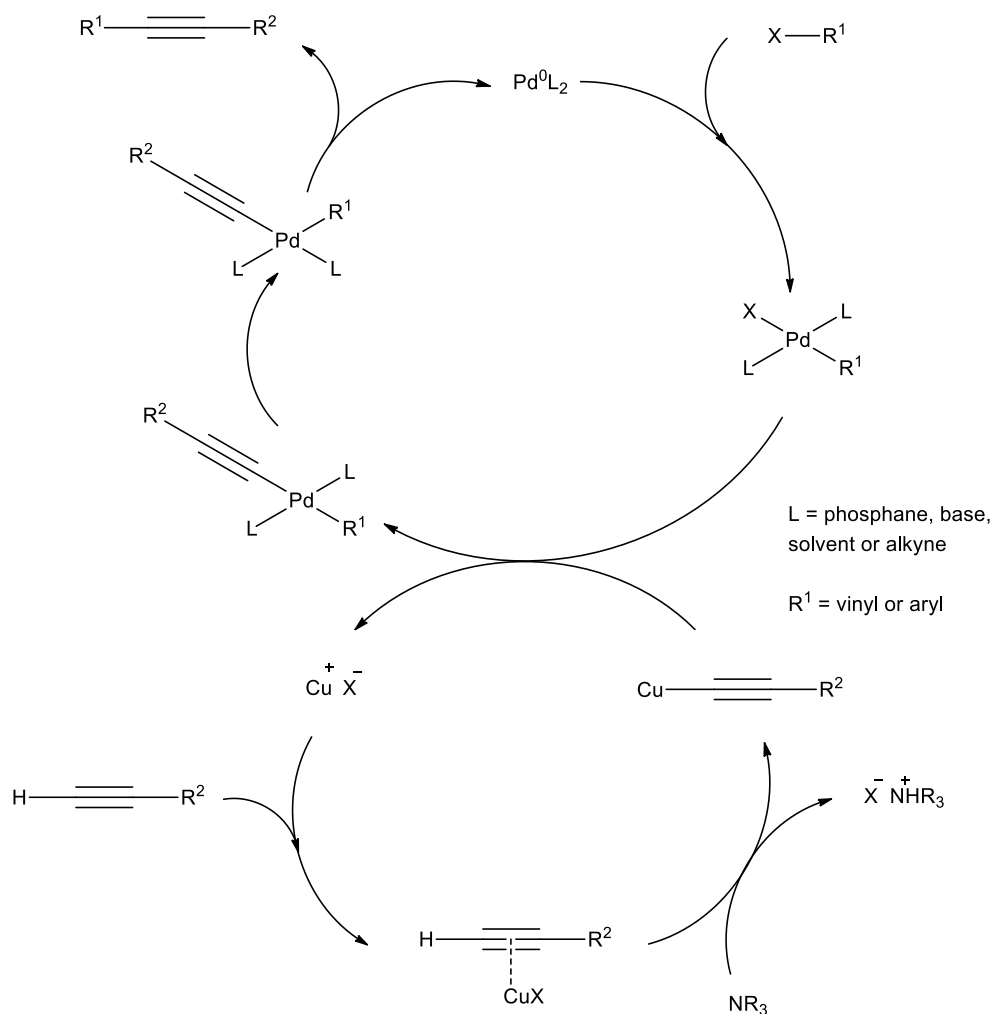
3.1.3 ALKYNYL–CARBYNE COMPLEXES

An alternative metal–ligand system with extended conjugation, which could be used to incorporate the ‘C≡P’ moiety, is that of the propargylidyne – metal complexes bearing an acetylenic chain with three carbon atoms. The first propargylidyne complex was prepared by Fischer *et al.*,²⁶¹ with the formation of $[\text{BrW}(\text{CO})_4(\equiv\text{C}-\text{C}\equiv\text{C}(\text{C}_6\text{H}_5))]$ by addition of BBr_3 to $[\text{W}(\text{CO})_5(=\text{C}(\text{OC}_2\text{H}_5)\text{C}\equiv\text{C}(\text{C}_6\text{H}_5))]$; synthetic methods to achieve such complexes are now fairly well-established. The synthetic route most commonly employed and predominantly developed by Stone²⁶² and Bruce²⁶³ involves reaction of $\text{M}(\text{CO})_6$ ($\text{M} = \text{Mo}, \text{W}$) with a lithiated terminal alkyne; subsequent reaction with trifluoroacetic anhydride (TFAA) at low temperature furnishes an acyl metallate *via* oxide abstraction, which subsequently rearranges to give the desired propargylidyne (Scheme 40). However, the instability of these metal–carbonyls can lead to decomposition. This can be circumvented by displacement of two carbonyls with a donor ligand, typically an amine, such as tmeda;^{264–268} such complexes demonstrate greater thermal stability due to increased electron density on the metal. While these complexes can be isolated, the lability of the acetyl/amine/CO ligands allows them to be displaced by a more stable spectator ligand such as hydrotris(pyrazolyl)borates ($\text{Tp}' = \text{Tp}, \text{Tp}^*$, Scheme 40).^{263,262,269} Although some complexes of this kind are known, there are no examples with the requisite propargylic terminal groups suitable for phosphaaalkyne synthesis, *i.e.* a carboxylic acid derivative.



Scheme 40: Formation of Group 6 propargylidyne complexes stabilised by Tp' ligands²⁶³

In order to install desirable termini to the propargylidyne chain for the purposes of phosphalkene formation, cross-coupling reactions have recently been utilised.^{270,271} The Sonogashira coupling is of particular interest, as it is used to form a C–C bond between sp^2 - and sp -hybridised carbon centres, generally an aryl or vinyl halide with a terminal alkyne. The reaction is catalysed by a Pd^0L_2 complex – generated *in situ* from a Pd^0 or Pd^{II} precatalyst – with CuI as a co-catalyst in the presence of an amine or inorganic base. The palladium complex undergoes an oxidative addition of the aryl or vinyl halide; at the same time, a copper acetylide complex is formed. The latter process is poorly understood, but it is thought to be assisted by an intermediate π -alkyne copper complex, which causes the proton of the terminal alkyne to become more acidic, allowing deprotonation by the amine.²⁷² Transmetalation then allows formation of a palladium acetylide, followed by a *cis/trans* isomerization, and finally a reductive elimination of the coupled product (Scheme 41).²⁷²

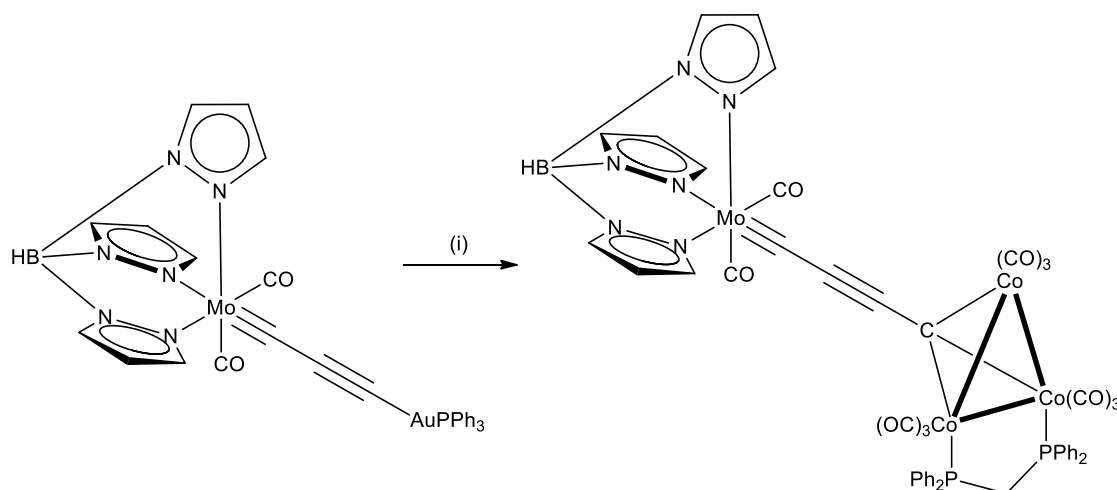


Scheme 41: Generic scheme of a Sonogashira cross-coupling reaction catalysed by a Pd⁰ complex and CuX.

This type of coupling has been applied in the pursuit of extended conjugated carbyne chains, the first example of which was achieved by reaction of $[\text{WCl}(\text{CO})_2(\text{tmeda})(\equiv\text{CC}_6\text{H}_4\text{I})]$ with $\text{HC}\equiv\text{CC}_6\text{H}_5$ and catalytic amounts of $\text{PdCl}_2(\text{PPh}_3)_2$ (5 mol%) and CuI (20 mol%).²⁷³ Heating the reagents in THF with an excess of KOH allowed formation of $[\text{WCl}(\text{CO})_2(\text{tmeda})(\equiv\text{C}(\text{C}_6\text{H}_4)\text{C}\equiv\text{C}(\text{C}_6\text{H}_5))]$. However, extending this reactivity to pre-existing propargylidynes with the aim of installing a particular functional group would require a propargylidyne with a terminal CH group, *i.e.* 'M $\equiv\text{CC}\equiv\text{CCH}$ ', of which there are no examples to date.

In recent years, the Sonogashira reaction has been successfully modified to circumvent the need for a terminal alkyne through the use of an $[\text{Au}(\text{PR}_3)]^+$ terminus, this fragment being isolobal with $[\text{H}]^+$.^{263,270,271,274,275} This method also circumvents the need for a base, which might potentially react preferentially with other ligands; when an $[\text{Au}(\text{PR}_3)]^+$ terminus is present, the

copper acetylide is formed directly *via* transmetalation. Particularly relevant examples of gold terminated propargylidyne are those described by Hill²⁷¹ and Bruce²⁶³ – $[\text{Tp}^*\text{W}(\text{CO})_2(\equiv\text{CC}\equiv\text{CAu}(\text{PPh}_3))]$ and $[\text{TpMo}(\text{CO})_2(\equiv\text{CC}\equiv\text{CAu}(\text{PPh}_3))]$, respectively. Both complexes were obtained from the respective silyl terminated propargylidyne $[\text{TpM}(\text{CO})_2(\equiv\text{CC}\equiv\text{CSiMe}_3)]$, though differing methods of desilylation were employed to install the $\text{Au}(\text{PPh}_3)_3$ terminus. Hill's approach involved addition of TBAF, while Bruce *et al.* used K_2CO_3 in a 4:1 THF/MeOH solvent mixture, with yields of 72% and 88%, respectively. These complexes were then used to add functionality to the propargylidyne, with Bruce able to show that addition of RX to the gold terminated propargylidyne under typical Sonogashira-type conditions led to the formation of $\text{AuX}(\text{PPh}_3)$ and a propargylidyne terminating in R such as that in Scheme 42. The first example of this reactivity was demonstrated by reaction of $[\text{Co}_3(\mu_3\text{-CBr})(\mu\text{-dppm})(\text{CO})_7]$ with the gold propargylidyne complex $[\text{TpMo}(\text{CO})_2(\equiv\text{CC}\equiv\text{CAu}(\text{PPh}_3))]$, with *ca.* 20 mol% $\text{Pd}(\text{PPh}_3)_4$ and CuI , furnishing the complex $[\{\text{Tp}(\text{OC})_2\text{Mo}\}\equiv\text{CC}\equiv\text{CC}\{\text{Co}_3(\mu\text{-dppm})(\text{CO})_7\}]$ (Scheme 42).



Scheme 42: Installation of a functional group at the terminus of a propargylidyne ligand *via* a gold cross-coupling reaction. *Reagents and Conditions:* (i) $[\text{Co}_3(\mu_3\text{-CBr})(\mu\text{-dppm})(\text{CO})_7]$, $\text{Pd}(\text{PPh}_3)_4$, CuI , THF, 2 h, r.t.

The various routes discussed, through which transition metal-terminated propargylidyne and alkynyls can be achieved, were each investigated with the aim of preparing a series of complexes that would be suitable precursors for phosphapolyynyl formation. These studies are discussed herein.

3.2 RESULTS AND DISCUSSION

3.2.1 SYNTHESIS OF Ru^{II}–ALKYNYL COMPLEXES

3.2.1.1 Attempted synthesis of $[RuH(CO)_2(PPh_3)_2(C\equiv CO_2H)]$

Complexes bearing the $C\equiv CCO_2H$ ligand were pursued in the first instance, as the carboxylic acid functionality could feasibly be converted to the acyl chloride, potentially enabling subsequent phosphalkene synthesis. While a number of main group alkynyl compounds terminating in a carboxylic acid are known,^{276,277} only one transition metal analogue exists, in the form of the rhodium compound $[RhH(N(C_2H_4PPh_2)_3)(C\equiv CCO_2H)][BPh_4]$;²⁷⁸ however, this complex was synthesised in admixture with the hydrido–carboxylate complex $[RhH(N(C_2H_4PPh_2)_3)(O_2CC\equiv CH)][BPh_4]$ due to competing oxidative addition pathways (C–H vs. O–H activation). While Marder *et al.* have demonstrated that C–H activation can occur exclusively, the $-C\equiv CCO_2H$ ligated compounds could not be isolated and were observed *in situ* during catalytic processes.^{279,280} Given the propensity for $[Ru(CO)_2(PPh_3)_3]$ (**17**) (Roper's Complex) to undergo oxidative addition (*vide supra*) in much the same way as the aforementioned rhodium complex, synthesis of $[RuH(CO)_2(PPh_3)_2(C\equiv CCO_2H)]$ was initially pursued.

Addition of a standard solution of $HC\equiv CCO_2H$ in DCM to a solution of $[Ru(CO)_2(PPh_3)_3]$ (**17**) in DCM at ambient temperature led to an intractable mixture of products. The 1H NMR spectrum of the crude product showed a doublet resonance at δ_H 10.33 ($J = 19.3$ Hz), consistent with an OH fragment, along with several doublet resonances consistent with vinylic protons between approximately δ_H 5.5 and 6.6. However, $^{31}P\{^1H\}$ NMR spectroscopy showed a complex mixture of products, which could not be separated by recrystallization.

The reaction was repeated in THF at ambient temperature for 1 h. A similar doublet resonance to that seen previously (δ_H 10.33) was observed at δ_H 10.47 ($J = 29.8$ Hz), with multiple resonances observed in the $^{31}P\{^1H\}$ NMR spectrum. In addition, two new multiplet resonances in the 1H NMR spectrum were observed at δ_H -6.82 (tdd, $J_{PH} = 30.9, 15.0$; $J_{HH} = 5.4$ Hz) and -8.84 (dtd, $J_{PH} = 73.6, 27.7$; $J_{HH} = 6.2$ Hz), integrating 1:1 and consistent with a metal bis-hydride species (Figure 25). The more shielded resonance at δ_H -8.84 presented one large and one small P–H coupling, with the larger coupling indicating that this hydride is *trans*- to a PPh_3 ligand; the smaller coupling suggests that it is *cis*- to at least one other PPh_3 ligand. The more deshielded resonance at δ_H -6.82 does not possess a large phosphorus coupling, indicating that it is not *trans*- to a PPh_3 ligand and that the two hydrides are not in the same plane. The smaller coupling, however, suggests that it is located *cis*- to one or more PPh_3 ligands.

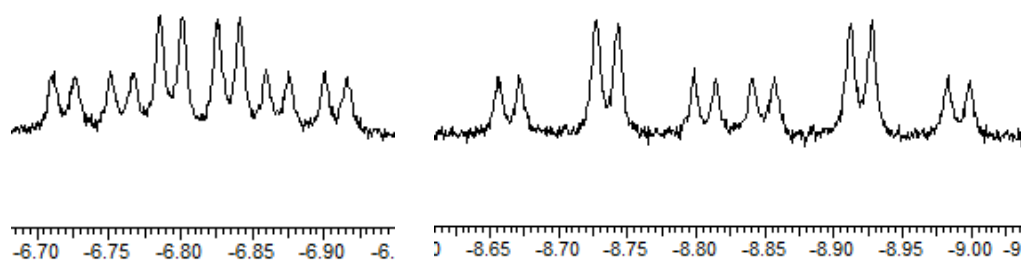
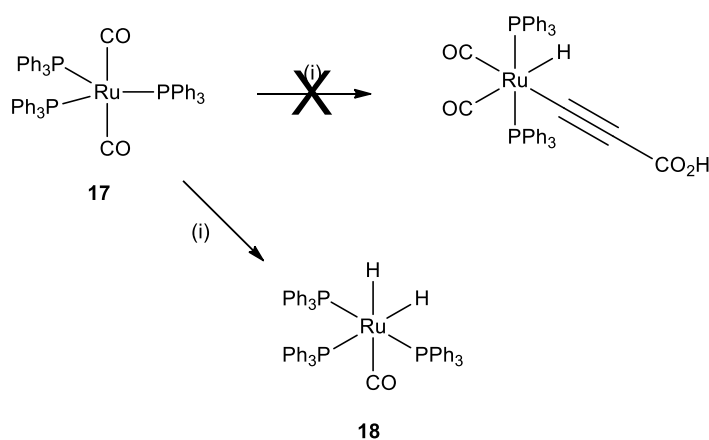


Figure 25: Hydridic proton resonances from the ^1H NMR spectrum of the crude product achieved *via* addition of $\text{HC}\equiv\text{CCO}_2\text{H}$ to **17**.

The complex was assigned as the known compound $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$ (**18**) (Scheme 43), reported by Wilkinson *et al.* and previously synthesised by the addition of NaBH_4 to a $\text{C}_6\text{H}_6/\text{EtOH}$ solution of **17** under a flow of H_2 .²⁸¹ NMR spectroscopic data were found to be in close agreement with those previously found by Wilkinson *et al.* ($\delta_{\text{H}} -8.67$, $J = 74, 29, 6$ Hz; $\delta_{\text{H}} -6.69$, $J = 30, 16$ Hz). Additionally, IR spectroscopy showed bands at 1966 cm^{-1} , 1908 cm^{-1} and 1935 cm^{-1} corresponding to two Ru–H and one CO stretch, respectively; again, this correlates closely with those previously reported by Wilkinson (ν_{RuH} 1900 cm^{-1} , 1960 cm^{-1} ; ν_{CO} 1940 cm^{-1}).

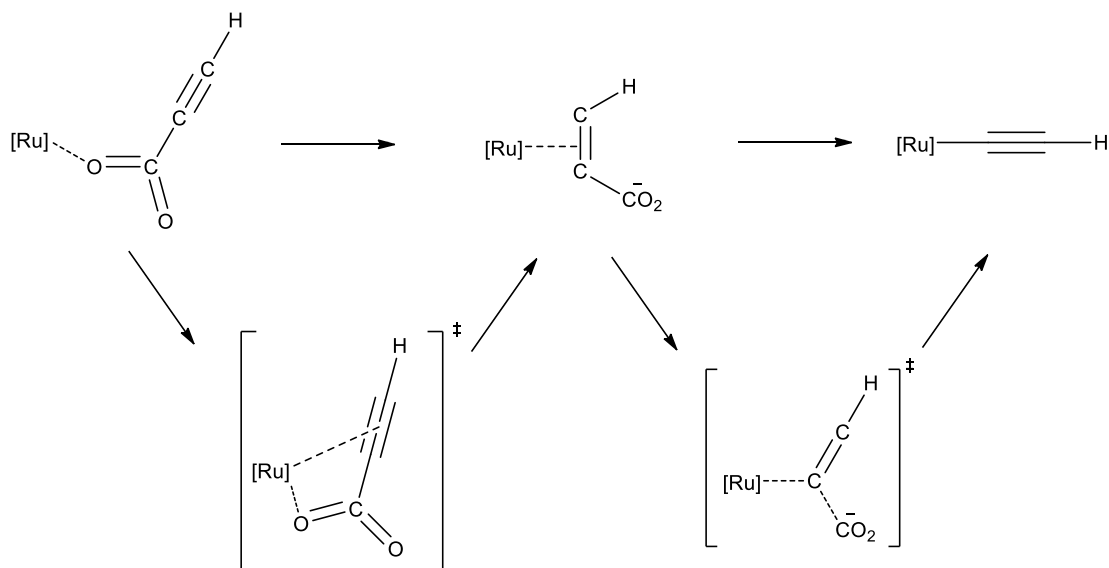


Scheme 43: Attempted synthesis of $[\text{RuH}(\text{CO})_2(\text{PPh}_3)_2(\text{C}\equiv\text{CCO}_2\text{H})]$ yielding the known complex **18**. *Reagents and Conditions:* (i) 2 $\text{HC}\equiv\text{CCO}_2\text{H}$, THF, 1 h, r.t.

To determine how hydride formation was occurring, whether by addition of C–H or O–H across the metal centre, $\text{TMS-C}\equiv\text{CCO}_2\text{H}$ was added to **17** at low temperature and allowed to warm to ambient temperature over the course of several hours. Metal hydride resonances were observed in the ^1H NMR spectrum of the resultant product mixture with two sharp triplets at $\delta_{\text{H}} -4.08$ ($J = 18.8$ Hz) and $\delta_{\text{H}} -4.39$ ($J = 19.1$ Hz) integrating in a 3:2 ratio, suggesting the formation of multiple products. Multiple resonances were observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum between

δ_p 44.5 and -5.4 , with the latter resonance indicating the presence of free PPh_3 . Infrared spectroscopy displayed bands at 2054 cm^{-1} , 1980 cm^{-1} and 1926 cm^{-1} , consistent with the $\text{C}\equiv\text{O}$ and two Ru-H bands.

With no terminal alkyne C-H bond to activate, the formation of multiple M-H containing products suggests that metal-hydride formation has occurred through the $-\text{CO}_2\text{H}$ functionality. Recent precedent for such O-H activations has been published by Bruce and co-workers, who synthesised $[\text{CpRu}(\text{dppe})(=\text{C}=\text{CH}_2)]$ from $[\text{CpRuCl}(\text{dppe})]$ and $\text{HC}\equiv\text{CCO}_2\text{H}$.²⁸² This was supported by DFT studies, which demonstrated that addition of $\text{HC}\equiv\text{CCO}_2\text{H}$ to the half-sandwich fragment “ $\text{CpRu}(\text{dppe})$ ” ($[\text{Ru}]$) occurs through initial coordination of $\text{HC}\equiv\text{CCO}_2^-$ and subsequent loss of CO_2 (Scheme 44). The resultant terminal alkyne is protonated at the β -carbon and rearranges to the allenyl product.

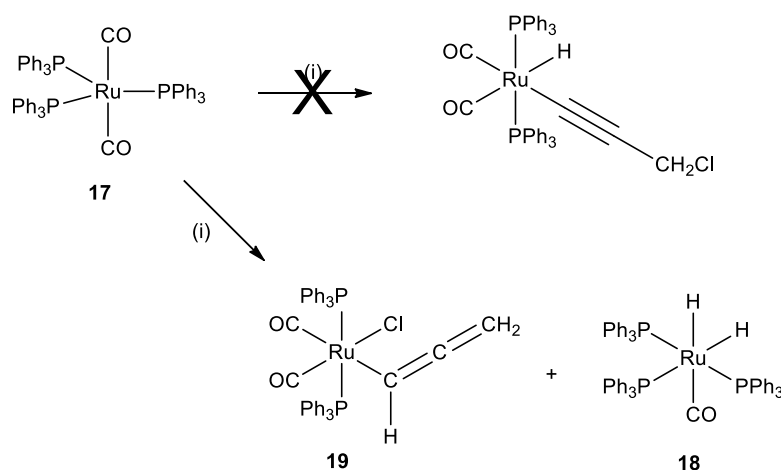


Scheme 44: Optimised pathway for the formation of $[\text{Ru}]-\text{CCH}$, leading to formation of $[\text{Ru}]=\text{C}=\text{CH}$ upon protonation, calculated using DFT ($[\text{Ru}] = \text{CpRu}(\text{dmpe})$).²⁸²

3.2.1.2 Attempted synthesis of $[\text{RuH}(\text{CO})_2(\text{PPh}_3)_2(\text{C}\equiv\text{CCH}_2\text{Cl})]$

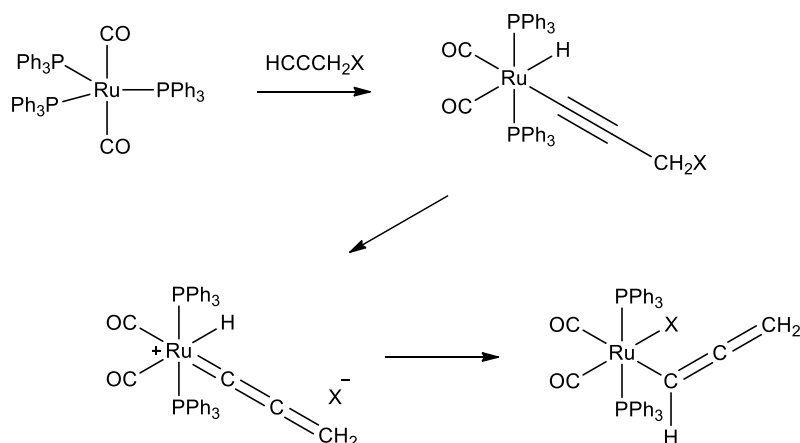
An alternative route toward the synthesis of the $-\text{C}\equiv\text{CC}\equiv\text{P}$ moiety requires generation of a Grignard reagent of the type $-\text{C}\equiv\text{CCH}_2\text{MgCl}$. With this in mind, complexes terminating in a $\text{C}\equiv\text{CCH}_2\text{Cl}$ functionality were also pursued. Again, while a number of main group analogues of such complexes have been synthesised,^{283–286} very few transition metal complexes terminating in a propargyl halide are known.^{246,247,287} The first example of this rare type of complex was the bis(alkynyl) Ni complex $[\text{Ni}(\text{PEt}_3)_2(\eta^1-\text{C}\equiv\text{CCH}_2\text{F})_2]$.²⁴⁵

Attempts to furnish $[\text{RuH}(\text{CO})(\text{PPh}_3)_2(\text{C}\equiv\text{CCH}_2\text{Cl})]$ involved addition of propargyl chloride to a solution of **17** in THF; however, a mixture of two products was formed. The dihydride $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$ (**18**) was once again observed, with multiplet resonances at δ_{H} -6.82 and -8.84 in the ^1H NMR spectrum (Figure 25). In addition, two significant new resonances were observed – multiplets at δ_{H} 5.54 and 3.46 integrating 1:2, respectively. These data correlate closely with those of the allenyl compound $[\text{RuBr}(\text{CO})_2(\text{PPh}_3)_2(\text{CH}=\text{C}=\text{CH}_2)]$ (CH, m, δ_{H} 5.70 ; CH_2 , m, δ_{H} 3.34), published by Hill *et al.*²⁵¹ and synthesised *via* addition of propargyl bromide to Roper's complex. On the basis of these data, it is likely that the hitherto unknown analogue $[\text{RuCl}(\text{CO})_2(\text{PPh}_3)_2(\text{CH}=\text{C}=\text{CH}_2)]$ (**19**) has been synthesised herein (Scheme 45). This is further supported by similar IR bands (ν_{CO} : 2038 , 1980 cm^{-1} (Cl, **19**); ν_{CO} : 2041 , 1981 cm^{-1} (Br)). Compounds **18** and **19** were synthesised in a 2:1 ratio respectively as observed by ^1H NMR spectroscopy.



Scheme 45: Attempted synthesis of $[\text{RuH}(\text{CO})(\text{PPh}_3)_2(\text{C}\equiv\text{CCH}_2\text{Cl})]$, yielding compounds **18** and **19**. *Reagents and Conditions:* (i) $2\text{ HC}\equiv\text{CCH}_2\text{Cl}$, THF, 1 h, r.t.

Hill *et al.* postulated that the mechanism of formation proceeds *via* initial oxidative addition of the alkynic C–H, yielding a metal–hydride intermediate. Subsequent formation of an allenylidene intermediate through dissociation of Br^- , followed by migratory coupling of the hydride with the allenylidene fragment eventually yields the allenyl product (Scheme 46).



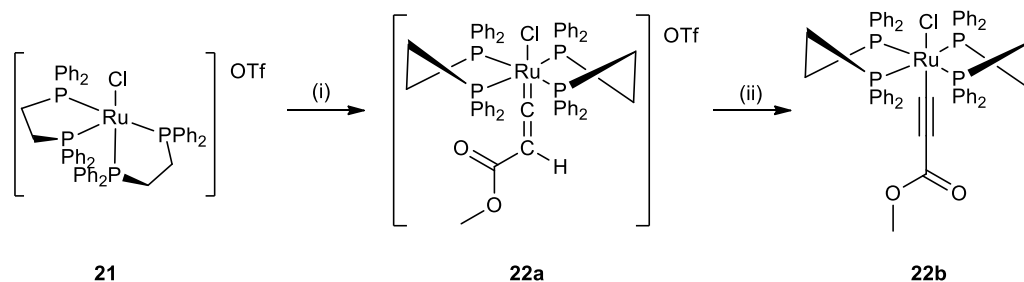
Scheme 46: General scheme for the formation of an allenyl product upon addition of a propargyl halide to **17**.

3.2.1.3 Synthesis of compounds of the type *trans*-[RuCl(dppe)₂(C≡CR)] and *trans*-[RuCl(dppe)₂(C≡CC₆H₄R')]

The reaction of RuCl₃·3H₂O with PPh₃ and subsequent addition of dppe furnished *trans*-[RuCl₂(dppe)₂] (**20**). The triflate salt [RuCl(dppe)₂][OTf] (**21**) was obtained by addition of 1 equivalent of AgOTf and the resultant product filtered and dried under reduced pressure, following literature procedures.²⁶⁰ The resultant product was characterized by multiplet resonances at 84.7 and 57.4 in the ³¹P{¹H} NMR spectrum, with the multiplicity due to a distorted trigonal bipyramidal structure.

Synthesis of the complex *trans*-[RuCl(dppe)₂(=C=CHCO₂Me)][OTf] (Scheme 47, **22a**) was initially attempted following procedures detailed by Low *et al.* for the synthesis of analogous complexes.²⁶⁰ HC≡CO₂Me and **21** in a 1:1 ratio were dissolved in DCM at ambient temperature for 1 h to obtain the desired vinylidene complex, however, this approach met with limited success. A singlet resonance in the ³¹P{¹H} NMR spectrum at *ca.* δ_P 40 was observed, in line with analogous vinylidene complexes, each displaying a single dppe phosphorus resonance at *ca.* δ_P 40–50.^{248–250} This change in chemical environment of the dppe phosphorus atoms from those of **21**, resulting in a singlet resonance, is due to the change in geometry from a distorted trigonal bipyramidal to an octahedral structure, with the dppe ligands defining the equatorial plane and Cl[−] and RC≡C[−] lying axial.²⁶⁰ Thus, this was thought to be consistent with formation of **22a**, however, resonances attributable to the presence of **21** were persistent. Preparative methods outlined by Dixneuf and coworkers²⁵⁸ suggested that 2 equivalents of alkyne were required in the formation of analogous PF₆[−] salts; therefore, 2 equivalents of HC≡CCO₂Me were

added to a solution of **21** in DCM and stirred under ambient conditions for 16 h, leading to the successful synthesis of pure **22a**.



Scheme 47: Synthesis of **22a** and **22b**; Reagents and Conditions: (i) 2 HC≡CCO₂Me, DCM, 16 h, r.t.; (ii) 2 KO^tBu, MeOH, r.t.

Formation of the vinylidene was further supported by a quintet at δ_{H} 3.42 ($^4J_{\text{HP}} = 2.4$ Hz) in the ^1H NMR spectrum, corresponding to a vinylic proton coupling to all four phosphorus centres. This is supported by a highly deshielded, broad carbon resonance, assigned to the Ru=C carbon centre, observed at δ_{C} 341.6 in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum; again, these data are in good agreement with those of related compounds. Additionally, proton resonances were observed at δ_{H} 3.06 (3H) and 2.84 (8H), indicating retention of the methyl ester functionality and dppe ligands, respectively.

Following the synthesis and isolation of **22a**, addition of a methanolic solution of KO^tBu led to immediate deprotonation of the vinylidene, yielding the desired alkynyl complex as a pale yellow precipitate (Scheme 47, **22b**). A shift in the phosphorus resonance to δ_{P} 48.1 is consistent with the synthesis of **22b** and comparable to related compounds *trans*-[RuCl(dppe)₂(C≡CC₆H₄R)] (R = Me, OMe, CO₂Me; δ_{P} 50.1–50.9).²⁵⁵ This was further supported by ^1H NMR spectroscopy, with a singlet observed at δ_{H} 3.51, indicating retention of the methyl ester functionality; a resonance corresponding to a vinyl proton was no longer observed. Resonances in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, consistent with the Ru–C_α≡C_β carbon centres were also observed (C_α: δ_{C} 143.1; C_β: δ_{C} 107.2) and were in close agreement with those found for the related complex *trans*-[RuCl(dppm)₂(C≡CCO₂Me)] (C_α: δ_{C} 141.3; C_β: δ_{C} 105.7).²⁵⁸ A stretch in the IR spectrum at 2032 cm^{−1}, assigned to the C≡C bond, is again consistent with analogous compounds, with C≡C stretches typically observed in the range 2000–2100 cm^{−1}.

Crystals of **22b**²⁹¹ were obtained by slow-cooling of a saturated solution of **22b** in DCM (Figure 26, Table 11). The C≡C and Ru–C bond lengths for **22b** ($d_{\text{C}\equiv\text{P}}$ 1.136(5) Å; $d_{\text{Ru}-\text{C}}$ 1.876(6) Å) are

slightly shorter than those seen in analogous compounds, typically ranging from 1.16–2.25 Å and 1.9–2.0 Å, respectively.^{252,258,260,282,292,293} An Ru–C(5)–C(6) angle of 175.8(7)° is close to linear and typical of that seen for alkynic ruthenium complexes of this type. The four phosphorus atoms are bent slightly out of the equatorial plane (Cl–Ru–P(1, 2, 3, 4) 86.46(8)°, 81.25(8)°, 94.31(8)°, 98.66(8)°), similar to that reported by Low and co-workers (*ca.* 92°) for analogous compounds bearing a phenyl spacer in the alkyne chain. The Cl–Ru–C_{alkynyl} angle is close to linear at 177.8(2)° and in close agreement with related complexes (169°–179°).^{260,293}

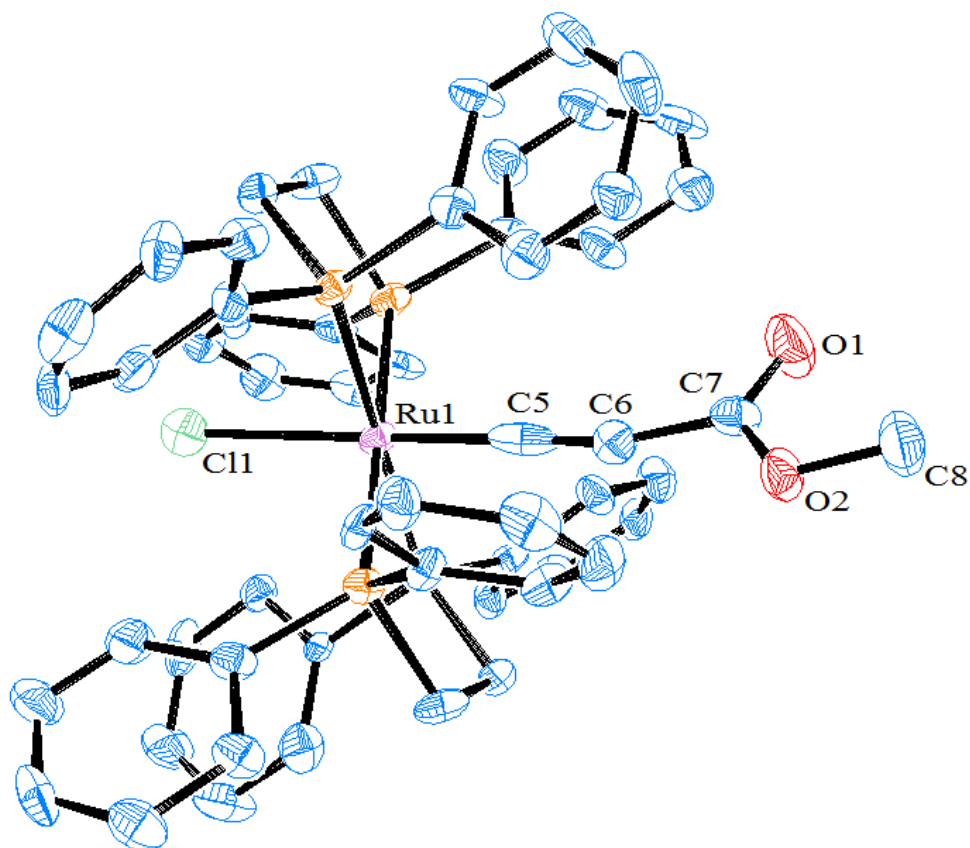


Figure 26: Molecular structure for **22b**. 50% thermal ellipsoids. H atoms omitted for clarity.

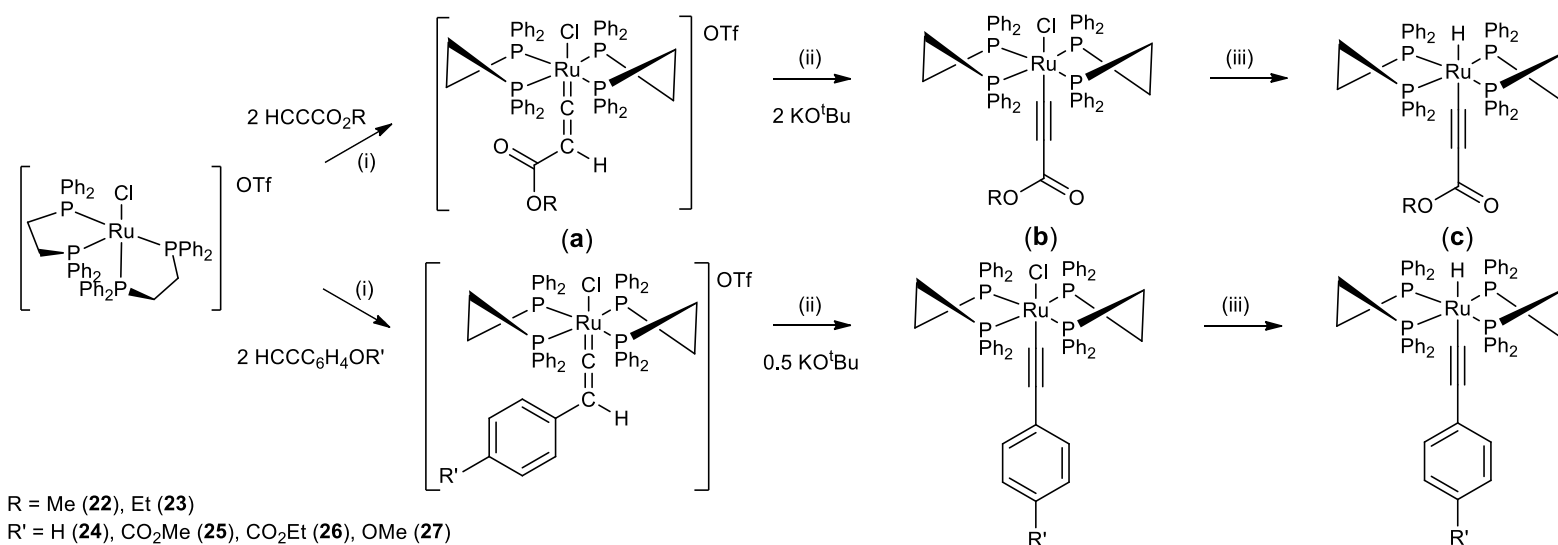
Table 11: Selected bond lengths (Å) and angles (°) for **22b**.

Ru(1)–Cl(1)	2.550(2)
Ru(1)–C(5)	1.876(6)
C(5)–C(6)	1.136(5)
C(5)–Ru(1)–Cl(1)	177.8(2)
C(6)–C(5)–Ru(1)	175.8(7)

Synthesis of a number of analogous vinylidene and alkynyl complexes was similarly achieved, with various functionalities ($R = \text{CO}_2\text{Et}$ (**23**); $R' = \text{H}$ (**24**), CO_2Me (**25**), CO_2Et (**26**), OMe (**27**); Scheme 48) – selected spectroscopic data are shown in Table 12. A trend towards greater shielding of the phosphorus centres in the vinylidene complexes (**a**) as compared to the alkynyl complexes (**b**) is observed, due to the greater σ -donating abilities of the vinylidene over the alkynyl, the latter participating more readily as a π -acceptor.²⁹⁴ The C_α atom of the vinylidene complexes is substantially more deshielded than C_β (δ_C *ca.* C_α : 300; C_β : 100); upon deprotonation to the alkynyl, C_α resonates at *ca.* δ_C 140 with little change in the relative frequency of C_β .

Both Low²⁶⁰ and Dixneuf²⁸⁸ found that an excess of base (KO^tBu or DBU) was required for conversion from vinylidene to alkynyl, for all compounds of the type $[\text{RuCl}(\text{dppe})_2(=\text{C}=\text{CHR})]$ where R is a variety of aryl, alkyl and silyl groups; however, when the dppe ligands were replaced with dppm ligands, only 1 equivalent of DBU was required.²⁵⁸ Interestingly, and in contrast to literature reports, the quantity of KO^tBu required for vinylidene to alkynyl conversion in this work varied according to the alkynyl functional group. Terminal groups with an aryl spacer required only $\frac{1}{2}$ an equivalent of KO^tBu yet unreacted vinylidene was not observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the resultant alkynyl compounds. This suggests that complete conversion to the ruthenium–alkynyl complexes was achieved, which is further supported by yields as high as 90%. Thus, a catalytic mechanism appears likely.

In each case, when the specific base requirements outlined above were exceeded, a second phosphorus containing product was formed, with a singlet resonance at *ca.* δ_P 60 observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum and a quintet at *ca.* δ_H –10 in the ^1H NMR spectrum. These data are consistent with formation of the hydride species $[\text{RuH}(\text{dppe})_2(\text{C}\equiv\text{CR})]$ ($R = \text{CO}_2\text{Me}$ (**22c**), CO_2Et (**23c**)) and $[\text{RuH}(\text{dppe})_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{R}')] (R' = \text{H}$ (**24c**), CO_2Me (**25c**), CO_2Et (**26c**), OMe (**27c**)). The mixture of chloride and hydride species formed was inseparable in all cases, however, upon addition of an excess of base in MeOH, 100% conversion to the hydride could be achieved after stirring under ambient conditions for 16 h (compounds **22–27(c)**, Scheme 48). Three such metal–hydride complexes have been previously reported ($R = \text{CO}_2\text{Me}$, Ph and ^nBu) and were accessed *via* the ammonia complexes $[\text{Ru}(\text{NH}_3)(\text{dppe})_2(\text{C}\equiv\text{CR})]$ by addition of NaOMe in MeOH.²⁰⁵ The mechanism of hydride formation was believed to be a result of displacement of the labile NH_3 ligand by methoxide, with subsequent β -elimination; a similar mechanism appears likely in the present case, given the lability of the chloride ligand.



Scheme 48: Synthesis of compounds **22–27(a–c)**; *Reagents and Conditions*: (i) DCM, 16 h, r.t.; (ii) DCM, MeOH, r.t.; (iii) xs. KO^tBu, DCM, MeOH, 16 h, r.t.

Table 12: Selected ³¹P{¹H} (161.7 MHz), ¹H NMR (399.5 MHz) NMR data (ppm) and *J*-couplings (Hz) for vinylidene (**a**), alkyne (**b**) and hydride (**c**) compounds **22–27** (Scheme 48) in CDCl₃.[‡]

		22	23	24	25	26	27
a	δ _H =CH (⁴ <i>J</i> _{HP})	3.42 (2.4)	3.37 (2.6)	3.31 (2.4)	4.48 (2.7)	4.63 (2.6)	3.73
	δ _P	40.1	40.6	39.4	36.1	36.1	38.4
b	δ _P	48.1	48.2	49.6	49.0	49.1	49.0
c	δ _H Ru–H (² <i>J</i> _{HP})	–9.88 (19.6)	–9.92 (19.9)	–10.28 (20.2)	–10.06 (19.7)	–10.05 (19.8)	–10.37 (19.8)
	δ _P	68.0	68.0	68.5	68.5	68.5	68.5

[‡] Compounds **22c**, **24b/c**, **25a/b**, **27a/b** were prepared by modified literature procedures.^{93,205,101}

To extend this work, the addition of $\text{C}\equiv\text{CCH}_2\text{Cl}$ was attempted. Addition of 2 equivalents of $\text{HC}\equiv\text{CCH}_2\text{Cl}$ to a solution of $[\text{RuCl}(\text{dppe})_2][\text{OTf}]$ led to formation of the vinylidene complex $[\text{RuCl}(\text{dppe})_2(\text{C}=\text{CHCH}_2\text{Cl})][\text{OTf}]$ (**28a**), with a singlet phosphorus resonance observed at δ_{P} 41.5, consistent with those found for complexes **22–27(a)**, in addition to a highly deshielded carbon resonances at δ_{C} 345.8. Formation of **28a** was further supported by resonances in the ^1H NMR spectrum at δ_{H} 3.06 (d, $^3J_{\text{HH}} = 9.2$) and δ_{H} 2.64 (tqnt, $^3J_{\text{HH}} = 9.2$ Hz, $^4J_{\text{HP}} = 2.7$ Hz), consistent with the CH_2 and CH protons, respectively; bulk purity was confirmed by elemental analysis. Attempts to synthesise and isolate the respective alkynyl with 100% purity met with limited success. Addition of 2 equivalents of KO^tBu to **28a** led to a mixture of products, with resonances in the $^{31}\text{P}\{^1\text{H}\}$ spectrum at δ_{P} 70.0 and 50.9 consistent with formation of the desired compounds $[\text{RuCl}(\text{dppe})_2(\text{C}\equiv\text{CCH}_2\text{Cl})]$ and $[\text{RuH}(\text{dppe})_2(\text{C}\equiv\text{CCH}_2\text{Cl})]$, respectively. However, an additional impurity was also observed with a resonance at δ_{P} 46.2. Upon repeating the reaction with an excess of KO^tBu and continual stirring at ambient temperature for 16 h, the two products were still observed in admixture.

3.2.1.4 Attempted synthesis of bis(alkynyl) complexes $[\text{Ru}(\text{dppe})_2(\text{C}\equiv\text{CR})(\text{C}\equiv\text{CR}')] (R=R' \text{ and } R\neq R')$

While numerous bis(alkynyl) complexes of the type $[\text{Ru}(\text{dppe})_2(\text{C}\equiv\text{CR})_2]$ have been reported in the literature, synthetic methods to achieve them include metathesis reactions with stannylalkynyl complexes of the type $\text{R}_3\text{SnC}\equiv\text{CR}'$ with a catalytic quantity of CuI , suggesting that synthesis of these compounds is not facile.^{295,296} However, Touchard and co-workers were able to produce a series of such complexes by addition of alkyne, NaPF_6 and NEt_3 to $[\text{RuCl}_2(\text{dppe})_2]$, with *in situ* deprotonation of the bis(vinylidene). Extending this method further, they were able to synthesise bis(alkynyls) from the mono(vinylidene) complexes $[\text{RuCl}(\text{dppe})_2(\text{C}=\text{CHR})][\text{PF}_6]$, again by addition of alkyne, NaPF_6 and NEt_3 , with *in situ* deprotonation.^{288,290,297} It was noted however, that use of a non-coordinating anion was required for such transformations. The pursuit of bis(acetylide) compounds of the type $[\text{Ru}(\text{dppe})_2(\text{C}\equiv\text{CCO}_2\text{R})_2]$ ($\text{R} = \text{Me}, \text{Et}$) is discussed herein, following similar methodology to that used in the successful synthesis of the mono(alkynyls) described in Section 3.2.1.3.

To a solution of $[\text{RuCl}_2(\text{dppe})_2]$ (**20**) in DCM was added 2 equivalents of AgOTf , resulting in an immediate colour change from yellow to red. After stirring for 5 min at ambient temperature, 4 equivalents of $\text{HC}\equiv\text{CCO}_2\text{Me}$ were added (*vide supra*) and the mixture left to stir for 16 h, with gradual formation of a green/brown precipitate observed. The mixture was filtered and the solid product dried under reduced pressure. A new product was observed by $^{31}\text{P}\{^1\text{H}\}$ NMR

spectroscopy (**F-1**) exhibiting four phosphorus resonances with complex multiplicity (Figure 27). This is consistent with four dppe phosphorus atoms in different chemical environments suggesting rearrangement of the ligands. This is likely to have occurred due to abstraction of both chloride ligands before addition of alkyne. Repeating the reaction with $\text{HC}\equiv\text{CCO}_2\text{Et}$ led to synthesis of an analogous product (**F-2**) with a similar $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (Table 13). A resonance at *ca.* δ_{P} 61 was observed in both spectra with very large J_{PP} couplings at around 235 Hz. As previously discussed in Section 2.5.3, such large J_{PP} couplings can occur between two phosphorus atoms in a *trans*- position relative to one another across a metal centre.

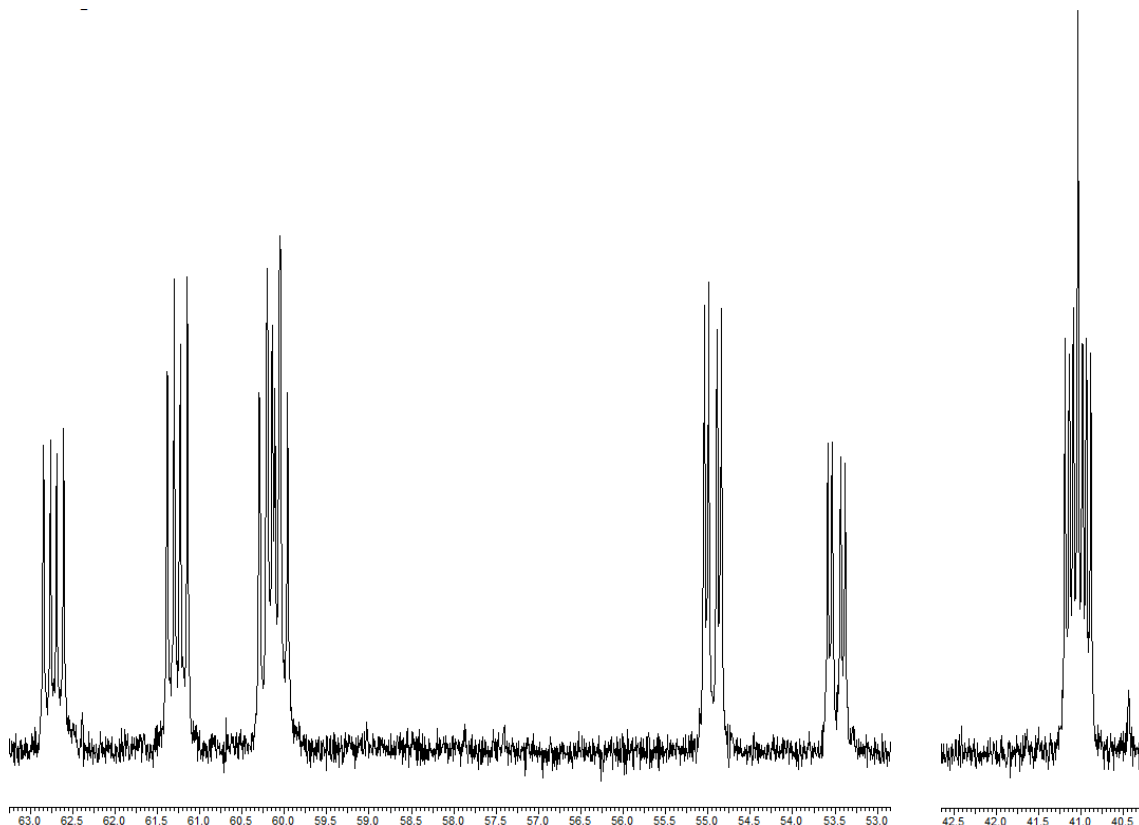


Figure 27: Selected phosphorus resonances from the $^{31}\text{P}\{^1\text{H}\}$ (161.7 MHz) NMR spectrum of **F-2** upon addition of 2 AgOTf to **20** with subsequent addition of 4 $\text{HC}\equiv\text{CCO}_2\text{Me}$, in CDCl_3 .

Table 13: $^{31}\text{P}\{^1\text{H}\}$ (161.7 MHz) NMR spectroscopic data for unknown species **F-1** and **F-2** upon addition of $\text{HC}\equiv\text{CCO}_2\text{Me}$ and $\text{HC}\equiv\text{CCO}_2\text{Et}$ to **20**, respectively, in CDCl_3

F-1			F-2		
δ_{P}	61.5	$J_{\text{PP}} = 235, 25.1, 13.9$	δ_{P}	62.0	$J_{\text{PP}} = 236, 25.1, 13.9$
	60.3	$J_{\text{PP}} = 23.4, 15.6, 13.9$		60.1	$J_{\text{PP}} = 25.1, 15.6, 13.9$
	55.5	$J_{\text{PP}} = 235, 23.4, 8.7$		54.2	$J_{\text{PP}} = 236, 24.3, 8.7$
	40.9	$J_{\text{PP}} = 25.1, 15.6, 8.7$		41.0	$J_{\text{PP}} = 25.1, 15.6, 8.7$

A ^1H NMR spectrum of complex **F-2** shows multiple resonances for the dppe protons and the presence of excess free alkyne. A triplet resonance corresponding to the CH_3 group of the ethyl fragment is observed at δ_{H} 1.20 ($^3J_{\text{HH}} = 7.14$ Hz). However, notably, the CH_2 group is observed as two doublet of quintet resonances at δ_{H} 4.00 and 3.78 ($J = 10.3, 7.1$ Hz), suggesting that the two protons are inequivalent and coupling to one another; this is supported by HSQC experiments that demonstrate both resonances interacting with the same carbon centre (δ_{C} 64.6).

The ^1H NMR spectrum also displays a doublet resonance at δ_{H} 9.42 ($J = 5.3$ Hz), integrating to one proton with respect to the ethyl fragment and showing an interaction with only two of the phosphorus resonances (δ_{P} 60.1 and 41.0). The relative shift and integration of this resonance is consistent with the proton of an aldehyde fragment. Indeed, this proton shows an interaction with a carbon resonance at δ_{C} 203.7 in an HSQC experiment, consistent with a $\text{C}(\text{H})=\text{O}$ carbon centre. This is further supported by a strong stretch in the IR spectrum of **F-2** at 1717 cm^{-1} .²⁹⁸ An interaction is also observed between this proton and a carbon resonance at δ_{C} 171.8 in a $^{13}\text{C}/^1\text{H}$ -HMBC experiment, with a second carbon resonance observed at δ_{C} 152.8. Neither resonance shows any interaction in a $^{13}\text{C}/^1\text{H}$ -HSQC experiment, suggesting retention of a C–C multiple bond.

Interaction between the aldehydic proton and only two of the phosphorus resonances suggests that this fragment is in some way associated with one of the dppe ligands, but not the other. Indeed, with all four phosphorus resonances in different environments it might be inferred that one of the phosphorus centres is no longer tethered to the metal centre. Bonding between this phosphorus centre and the C–C multiple bond would go some way to explain the discrepancies in the data and would imply the presence of a C=C alkenic fragment. However, with the data available and in lieu of X-ray diffraction data, the connectivity of this molecule is difficult to conclude unambiguously.

An alternative route to preparing the desired compounds of type $[\text{Ru}(\text{dppe})_2(\text{C}\equiv\text{CO}_2\text{R})_2]$ involved mixing of the alkyne and $[\text{RuCl}_2(\text{dppe})_2]$ (**20**) prior to AgOTf addition, *i.e.* the reagents were added in the reverse order to that above. To a solution of **20** in DCM were added 4 equivalents of $\text{HC}\equiv\text{CCO}_2\text{Et}$ before addition of 2 equivalents of AgOTf. One singlet resonance was observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the subsequent product at δ_{P} 40.4, consistent with vinylidene formation. However, resonances in the ^1H NMR spectrum were identical to those of the mono-vinylidene complex $[\text{RuCl}(\text{dppe})_2(\text{C}=\text{CHCO}_2\text{Et})][\text{OTf}]$ (**23a**), with ethyl resonances in a 1:1 ratio with respect to the dppe protons; the presence of excess $\text{HC}\equiv\text{CCO}_2\text{Et}$ was also apparent. Additionally, whilst mass spectrometry indicated the presence of the “ $\text{Ru}(\text{dppe})_2(\text{C}=\text{CHCO}_2\text{Et})$ ” fragment, the molecular ion peak for the bis(vinylidene) was not

observed. Formation of the mono-vinylidene was further supported upon addition of KO^tBu , with the synthesis of both the mono-alkynyl chloride and hydride complexes (**23b** and **23c**, respectively), observed by $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectroscopy. Similar results were observed when attempting to access the analogous complex $[\text{Ru}(\text{dppe})_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{CO}_2\text{Me})_2]$. The aryl-alkyne, **20** and AgOTf were dissolved in DCM simultaneously, with formation of the mono-vinylidene complex $[\text{RuCl}(\text{dppe})_2(=\text{C}=\text{CHC}_6\text{H}_4\text{CO}_2\text{Me})][\text{OTf}]$ (**25a**) confirmed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, with a resonance at δ_{P} 36.1 and a broad multiplet at δ_{H} 4.48, integrating in a 1:8 ratio with the 8 dppe protons; these data are identical to those found for **25a**. Again, subsequent addition of KO^tBu led to formation of the mono-alkynyl chloride and hydride complexes (**25b** and **25c**, respectively). Over numerous repetitions of the reaction, with the order of addition of AgOTf and alkyne alternated, reactivity was seen to be consistent, *i.e.* when AgOTf was added first, compound **F-2** was formed preferentially and *vice versa*. **F-2** and **25a** were often observed in admixture, however, their relative proportions correlated with the order in which the reagents were added.

The effect of temperature on the formation of **F** vs. the mono-vinylidene complex was also explored. $\text{HC}\equiv\text{CCO}_2\text{Et}$ and **20** were dissolved in DCM in an IMS bath to maintain the temperature at 21 °C. Upon subsequent addition of AgOTf and stirring for 72 h, the expected mono-vinylidene complex was formed as the major product, with a very small amount of **F-2** observed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. However, upon repeating the reaction at 0 °C and allowing the mixture to warm to ambient temperature over 16 h, **F-2** was formed in far greater abundance than **25a**. Indeed, this same result was observed when repeating the reaction at -30 °C and again allowing the mixture to warm to 12 °C over 16 h. These observations are consistent with rearrangement of the dppe ligands prior to alkynyl addition, such that they no longer occupy the equatorial positions about the metal centre which they previously occupied in the octahedral starting material (**20**), meaning that each phosphorus centre is in a different chemical environment. This was believed to be plausible as at lower temperature, alkynyl addition might be slowed sufficiently that the ligands would have time to rearrange.

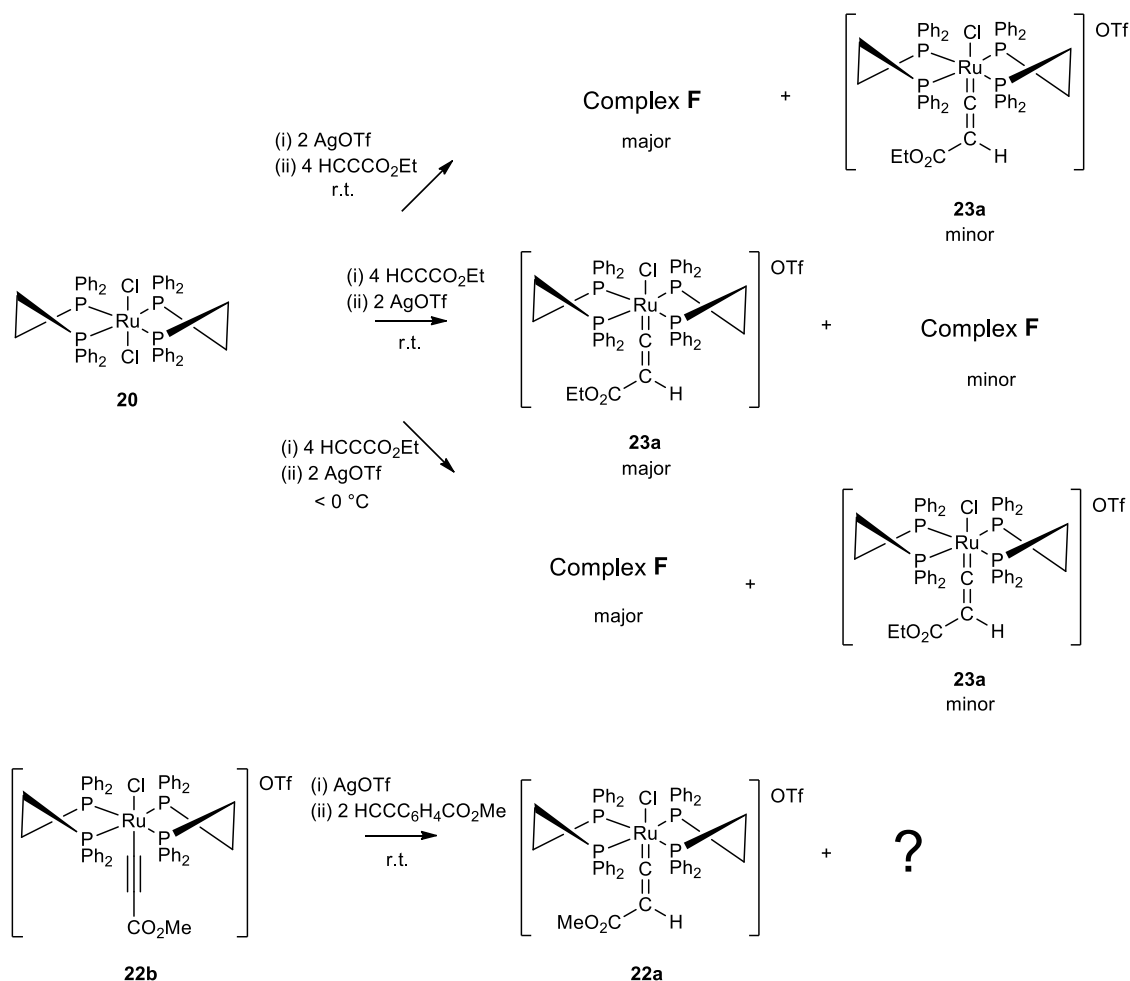


Figure 28: Attempted synthesis of bis(alkynyl) complexes of the type $[\text{Ru}(\text{dppe})_2(\text{C}\equiv\text{CO}_2\text{R})_2]$.

The mixed bis(alkynyl) complex $[\text{Ru}(\text{dppe})_2(\text{C}\equiv\text{CR})(\text{C}\equiv\text{CC}_6\text{H}_4\text{CO}_2\text{Me})]$ was also targeted. $\text{HC}\equiv\text{CC}_6\text{H}_4\text{CO}_2\text{Me}$, AgOTf and **20** in a 2:2:1 ratio were dissolved in DCM with immediate addition of 2 equivalents of $\text{HC}\equiv\text{CCO}_2\text{Me}$. After 16 h, a singlet resonance was observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at δ_{P} 39.8, consistent with formation of the mono-vinylidene $[\text{RuCl}(\text{dppe})_2(=\text{C}=\text{CHCO}_2\text{Me})][\text{OTf}]$ (**22a**), and the ^1H NMR spectrum showed the presence of excess $\text{HC}\equiv\text{CC}_6\text{H}_4\text{CO}_2\text{Me}$, again supporting the formation of **22a**; preferential addition of $\text{HC}\equiv\text{CCO}_2\text{Me}$ over $\text{HC}\equiv\text{CC}_6\text{H}_4\text{CO}_2\text{Me}$ had evidently occurred. These data were supported by resonances at δ_{H} 3.42 and 3.01, consistent with the vinylic and CH_3 protons respectively, with integrations of 1 and 3 relative to that of the dppe protons (m, δ_{H} 2.82). Upon addition of KO^tBu to the crude product, both the alkynyl and hydride complexes **22b** and **22c** were formed, with phosphorus resonances observed at δ_{P} 68.0 and 48.1. Evidently, only one Cl^- ligand of compound **20** is displaced under the above reaction conditions. Therefore, synthesis of $[\text{Ru}(\text{dppe})_2(\text{C}\equiv\text{CCO}_2\text{Me})(\text{C}\equiv\text{CC}_6\text{H}_4\text{CO}_2\text{Me})]$ was attempted by addition of AgOTf to the mono-

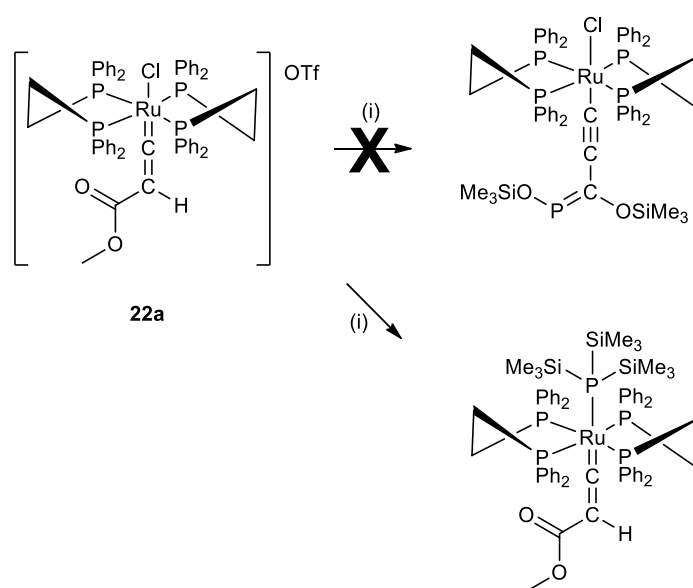
alkynyl $[\text{RuCl}(\text{dppe})_2(\text{C}\equiv\text{CCO}_2\text{Me})]$ (**22b**) in DCM, with subsequent addition of 1 equivalent of $\text{HC}\equiv\text{CC}_6\text{H}_4\text{CO}_2\text{Me}$. A mixture of products was observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, however, a resonance at δ_{P} 40.5 is consistent with protonation of the alkynyl species to the vinylidene **22a**, supported by proton resonances at δ_{H} 3.46, 3.12 and 2.86; moreover, upon addition of KO^tBu in MeOH the related hydride species $[\text{RuH}(\text{dppe})_2(\text{C}\equiv\text{CCO}_2\text{Me})]$ was formed.

3.2.1.5 Toward Installation of Phosphaalkene termini

Having successfully synthesised suitable precursors for phosphaalkene synthesis, namely compounds of the type $[\text{RuCl}(\text{dppe})_2(\text{C}\equiv\text{CR})]$ ($\text{R} = \text{CO}_2\text{Me}$ (**22b**), CO_2Et (**23b**), $\text{C}_6\text{H}_4\text{CO}_2\text{Me}$ (**25b**), $\text{C}_6\text{H}_4\text{CO}_2\text{Et}$ (**26b**)), conversion of the ester functionality to a the phosphaalkene $[\text{RuCl}(\text{dppe})_2(\text{C}\equiv\text{CC}(\text{OSiMe}_3)=\text{P}(\text{OSiMe}_3))]$ was attempted. A solution of $\text{LiP}(\text{TMS})_2$ in THF was added to a cooled solution of **22b** in THF and the mixture allowed to warm to ambient temperature. After 3 h, solvent was removed, however, no reaction had occurred with only **22b** observed in both the $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectra. The reaction was repeated in Et_2O , following a similar procedure to that of Weber *et al.*,⁸⁶ however, again, no reaction occurred with only clean starting material observed by NMR spectroscopy. The reaction was repeated with $\text{P}(\text{TMS})_3$ in dimethoxyethane (DME); DME was chosen as a solvent to allow for high reflux temperatures. An aliquot of the crude product was taken after 48 h at ambient temperature, however, NMR spectroscopy revealed only starting material. The reaction mixture was then heated to reflux for 4 h but again, no reaction was observed.

As complex **22b** appeared to be particularly unreactive, an excess of $\text{LiP}(\text{TMS})_2$ was added to the vinylidene precursor complex (**22a**). While the phosphide would clearly act as a base and deprotonate the vinylidene, it was hoped that in addition, attack at the carbonyl group would occur *in situ*; however, $\text{LiP}(\text{TMS})_2$ served only to efficiently deprotonate the vinylidene, with **22b** observed by NMR spectroscopy. However, when repeating the reaction with $\text{P}(\text{TMS})_3$, a new product was detected *via* NMR spectroscopy. Two resonances, a doublet and a quintet, were observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the resultant product, with mutual coupling (d, δ_{P} 48.8; qnt, δ_{P} -98.2; $J_{\text{PP}} = 27.34$ Hz). A ^1H NMR spectrum revealed a resonance consistent with OMe protons (δ_{P} 3.72) and a broad multiplet, integrating to 1 with respect to the methyl group and consistent with a vinylic proton (δ_{P} 3.58). These data suggest that the vinylidene fragment has been retained. A resonance at δ_{H} 0.29 integrating to 27 and a broad multiplet integrating to 8 at δ_{H} 2.76 are consistent with the presence of $\text{P}(\text{TMS})_3$ and retention of the dppe ligands, which suggests the loss of Cl^- . Given the obtained data, the complex might be

assigned as $[\text{Ru}(\text{dppe})_2\text{P}(\text{TMS})_3(=\text{C}=\text{CHCO}_2\text{Me})]$ (Scheme 49), which would be the first example of a $\text{Ru}-\text{P}(\text{TMS})_3$ fragment. However, other transition metal complexes bearing the $\text{P}(\text{TMS})_3$ ligand are known and while they are few in number, they all demonstrate phosphorus resonances close to that of the free $\text{P}(\text{TMS})_3$ (*ca.* $\delta_{\text{P}} -250$).^{299–301} The complex could alternatively be assigned as $[\text{Ru}(\text{dppe})_2\text{P}(\text{TMS})_2(=\text{C}=\text{CHCO}_2\text{Me})][\text{OTf}]$ with a $\text{P}(\text{TMS})_2$ ligand as complexes bearing the $\text{P}(\text{TMS})_2$ ligand have highly variable phosphorus chemical shifts ranging from $\delta_{\text{P}} -130$ to -20 , which is in better agreement with that observed in the present case. However, integration of the proton resonances in the ^1H NMR spectrum are not consistent with such a product. As such, the nature of this compound cannot be unambiguously determined at this stage.



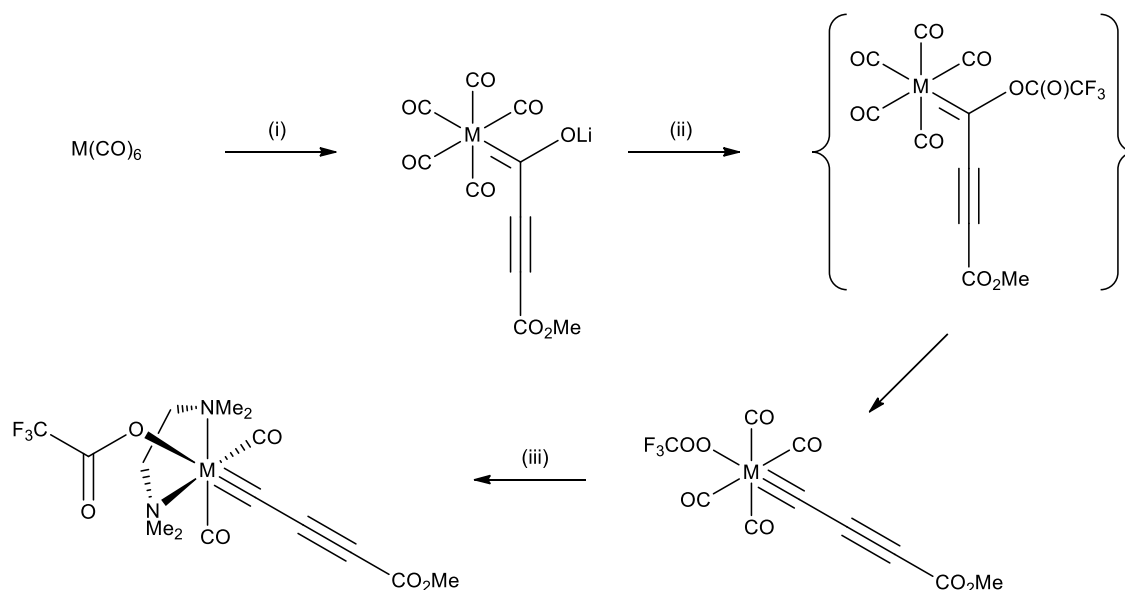
Scheme 49: Attempted synthesis of $[\text{RuCl}(\text{dppe})_2(\text{C}\equiv\text{CC}(\text{OSiMe}_3)=\text{P}(\text{OSiMe}_3))]$ by addition of $\text{P}(\text{TMS})_3$ to **22a**, leading to the synthesis of a new unknown species. *Reagents and Conditions:*

(i) $\text{P}(\text{TMS})_3$, THF, 2 h, r.t.

3.2.2 SYNTHESIS OF PROPARGYLIDYNE COMPLEXES

3.2.2.1 Propargylidyne via Acyl Metallates

The propargylidyne complexes $[\text{M}(\equiv\text{CC}=\text{CSiMe}_3)\{\text{OC}(\text{O})\text{CF}_3\}(\text{CO})_2(\text{tmeda})]$ ($\text{M} = \text{W},^{265} \text{Mo}^{263}$) have previously been synthesised *via* an acyl metallate intermediate (*vide supra*, Scheme 40). Attempts to synthesise the analogous compounds $[\text{M}(\equiv\text{CC}=\text{CCO}_2\text{Me})\{\text{OC}(\text{O})\text{CF}_3\}(\text{CO})_2(\text{tmeda})]$ ($\text{M} = \text{W}$ and Mo) were carried out following similar literature procedures (Scheme 50).



Scheme 50: Attempted synthesis of compounds $[M(≡CC≡CCO_2Me)\{OC(O)CF_3\}(CO)_2(tmeda)]$ ($M = W$ and Mo). *Reagents and Conditions*: (i) $LiC\equiv CCO_2Me$; (ii) $(CF_3CO)_2O$; (iii) $tmeda$.

$nBuLi$ was added to a solution of $HC\equiv CCO_2Me$ in THF at $-30\text{ }^\circ\text{C}$ and stirred for 20 min before addition of $W(CO)_6$; an immediate colour change to yellow was observed. The mixture was allowed to warm to ambient temperature over 1 h, with a gradual colour change to dark brown observed. The solution was cooled to $-80\text{ }^\circ\text{C}$ before drop-wise addition of $(CF_3CO)_2O$ and subsequently warmed to $-50\text{ }^\circ\text{C}$ before addition of $tmeda$; CO was evolved as expected, however, no colour change was observed upon addition of either reagent. The solution was allowed to warm to ambient temperature. An intractable mixture of products was observed in the 1H NMR spectrum. While the presence of $tmeda$ was evident, with resonances at δ_H 2.84 and 2.53 integrating 4:12, respectively, it would appear that it is not coordinated to the metal centre as might be expected. This conclusion is based on comparison with the complexes $[M(≡CC\equiv CSiMe_3)\{OC(O)CF_3\}(CO)_2(tmeda)]$ ($M = Mo, W$), which exhibit three $tmeda$ proton resonances in their 1H NMR spectra. Two further resonances were seen at δ_H 3.59 and 3.96 either of which might be attributed to the methyl ester CH_3 group. However, an additional resonance at δ_H 13.15 was observed, which might reasonably be attributed to a hydroxyl group, presumably the result of deesterification in the presence of a base.

Three additional, smaller resonances were observed at δ_H 3.32, 2.80 and 2.28, integrating 6:4:6 respectively, similar to those of $[Mo(≡CC\equiv CSiMe_3)\{OC(O)CF_3\}(CO)_2(tmeda)]$, which exhibits $tmeda$ resonances at δ_H 3.02, 2.80 and 2.60, in the same ratio. However, this minor product could not be isolated. Infrared spectroscopy of the mixture was ambiguous, showing a strong stretch at 1672 cm^{-1} corresponding to the $C=O$ bond of the trifluoroacetato group, however, the

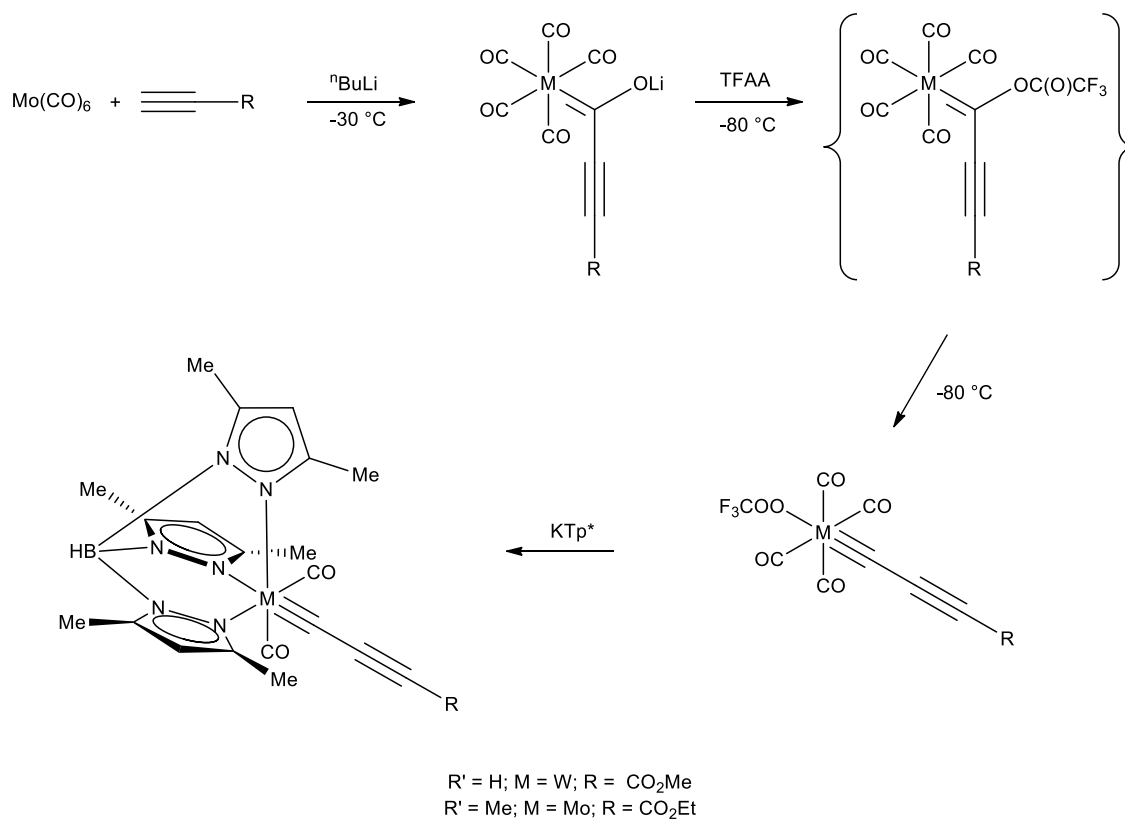
C≡O absorptions were difficult to assign, with only one broad, weak band at 1923 cm⁻¹ observed.

In view of the apparent deesterification, the conditions of the reaction were altered to prevent nucleophilic attack at the ester carbonyl group; thus, the initial lithiation step was carried out at -80 °C and allowed to stir for 30 min prior to addition of W(CO)₆. The ¹H NMR spectrum again showed tmeda resonances in a 4:12 ratio, with a slight shift in frequency to δ_H 2.91 and 2.57; however, a hydroxyl resonance was not observed in this instance. A resonance corresponding to the ester CH₃ group was not observed. Again, a minor product was observed with resonances at δ_H 3.40 and 2.31, integrating 1:1 – a third tmeda resonance was not observed, though was possibly obscured by other resonances. Numerous repetitions of the reaction under the same conditions demonstrated dramatically different ratios of the two products, with hydroxyl resonances appearing sporadically. As such, the nature of the products could not be ascertained. Attempts to prepare the molybdenum analogue were similarly unsuccessful.

It is possible that the inherent instability of complexes of the type [M(≡CC≡CSiMe₃){OC(O)CF₃}(CO)₂(tmeda)] may have hindered their synthesis and characterization. Thus, displacement of the carbonyl ligands with a tripodal ligand such as Tp and Tp* to furnish compounds of the type [Tp*M(CO)(≡CC≡CR)] (M = W and R = CO₂Me; M = Mo and R = CO₂Et) was attempted, following a modification of literature procedures.^{265,302} In order to furnish [Tp*W(CO)(≡CC≡CCO₂Me)], a 2.5 M solution of ⁿBuLi was added to a solution of HCCCO₂Me in THF at -80 °C; after 30 min, W(CO)₆ was added and the mixture allowed to warm to ambient temperature over 1 h. The resultant solution was cooled to -80°C before addition of (CF₃CO)₂O. The mixture was stirred at this temperature for 30 min to allow rearrangement of the acyl tungstate to the propargylidyne complex [W(CO)₄{OC(O)CF₃}(≡CC≡CCO₂Me)], signified by evolution of CO. KTp* was added before allowing the mixture to warm to ambient temperature over 1 h.

The ¹H NMR spectrum showed a complex mixture of products and while column chromatography led to a somewhat simpler product distribution, the species could not be identified. The reaction was repeated in similar fashion with Mo(CO)₆ and HCCCO₂Et; the latter reagent was chosen due to the more distinctive NMR resonances/couplings, in order to facilitate characterisation of the product. One Tp* containing product was observed in the ¹H NMR spectrum, with resonances at δ_H 6.15 and 5.73 in a 1:2 ratio, assigned to the H³ protons of the pyrazolyl ring, demonstrating a shift from that of the free ligand. Additional resonances at δ_H 2.57, 2.36 and 2.29, in a 3:12:3 ratio, were assigned to the Tp* CH₃ groups. However, despite this promising result, the ethyl protons of the alkynyl-carbyne ligand could not be identified,

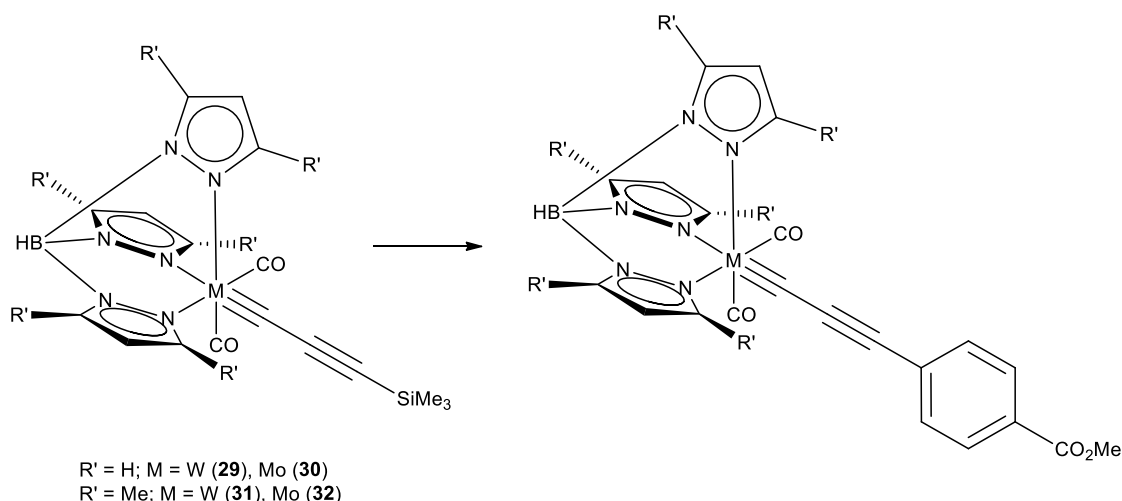
suggesting loss of the ester functionality. Further efforts to purify and isolate individual products proved unsuccessful.



Scheme 51: Attempted synthesis of compounds $[\text{Tp}^*\text{W(CO)(≡CC≡CCO}_2\text{Me)}]$ and $[\text{Tp}^*\text{Mo(CO)(≡CC≡CCO}_2\text{Et)}]$.

1.5.1.1 Toward installation of desirable termini to propargylidynes via Sonogashira coupling reactions

Coupling reactions present a potential alternative to synthesise propargylidynes with the desired terminal functionality, with the Sonogashira coupling reaction proven successful when applied to tungsten alkynylcarbyne complexes (*vide supra*). Therefore, coupling of the known compounds $[\text{Tp}'\text{M(CO)}_2(\text{≡CC≡CSiMe}_3)]$ ($\text{Tp}' = \text{Tp}$ and $\text{M} = \text{W}$ (**29**) and Mo (**30**); $\text{Tp}' = \text{Tp}^*$ and $\text{M} = \text{W}$ (**31**) and Mo (**32**)) with $\text{I(C}_6\text{H}_4\text{)CO}_2\text{Me}$ was attempted in an effort to obtain the complexes $[\text{Tp}'\text{M(CO)}_2(\text{≡CC≡C(C}_6\text{H}_4\text{)CO}_2\text{Me)}]$ ($\text{Tp}' = \text{Tp}$ and $\text{M} = \text{W}$ and Mo ; $\text{Tp}' = \text{Tp}^*$ and $\text{M} = \text{W}$ and Mo) (Scheme 52).



Scheme 52: Synthesis of compounds $[Tp'M(CO)_2(≡CC≡C(C_6H_4)CO_2Me)]$ ($Tp' = Tp$ and $M = W$ and Mo ; $Tp' = Tp^*$ and $M = W$ and Mo) under reaction conditions **I–XVIII**.

The known compounds **29–32** were synthesised *via* modified literature procedures. Subsequent reaction with an aryl halide was initially carried out under traditional Sonogashira-type conditions³⁰³ in pursuit of the desired complexes (summarised in Table 14) – $[Tp'M(CO)_2(C≡CCSiMe_3)]$, $I(C_6H_4)CO_2Me$, a large excess of triethylamine and 10 mol% of both $[PdCl_2(PPh_3)_2]$ and CuI were heated to 60 °C in dimethylformamide (DMF) before addition of a slight excess of TBAF (Table 14, reaction conditions **I–III**). The mixture was stirred for 2 h; however, for neither the tungsten nor molybdenum analogue was any reaction was observed under these conditions.

The reaction was repeated with **32** and the mixture heated to 60 °C for 16 h (Table 14, **IV**). This led to more promising results, with $I(C_6H_4)CO_2Me$ having been consumed. Whilst multiple minor products were observed in the 1H NMR spectrum, one major phenyl-containing species had formed. Resonances were observed in the aryl region at δ_H 8.14 and 8.12 ($J = 8.5$ Hz) integrating in a 1:1 ratio – this combined with a singlet resonance at δ_H 3.96 with an integration of 1.5 was consistent with the methyl benzoate functional group. However, the Tp^* ligand appeared to have been lost, with no discernible CH_3/CH resonances attributable to the ligand; it is therefore unclear as to what products were formed.

Table 14: Variations of Sonogashira Coupling Reactions Attempted with compounds **29–32** (Scheme 52) and $\text{IC}_6\text{H}_4\text{CO}_2\text{R}^{\S}$

	Propargylidyne Reagent	Temp.	Time (h) ^{**}	Pd Catalyst	CuI (mol%)	Pd Catalyst (mol%)	Solvent	Base	Desilylating Agent
I	30	60 °C	2	$\text{PdCl}_2(\text{PPh}_3)_2$	10	10	DMF	NEt_3	TBAF
II	32	60 °C	2	$\text{PdCl}_2(\text{PPh}_3)_2$	10	10	DMF	NEt_3	TBAF
III	31	60 °C	2	$\text{PdCl}_2(\text{PPh}_3)_2$	20	10	DMF	NEt_3	TBAF
IV	32	60 °C	16	$\text{PdCl}_2(\text{PPh}_3)_2$	10	10	DMF	NEt_3	TBAF
V	32	reflux	1 { 24 }	$\text{PdCl}_2(\text{PPh}_3)_2$	20	20	NEt_3	NEt_3	TBAF
VI	30	reflux	3 { 16 }	$\text{Pd}(\text{PPh}_3)_4$	10	20	MeOH/THF	K_2CO_3	K_2CO_3
VII	32	reflux	3 { 16 }	$\text{Pd}(\text{PPh}_3)_4$	10	10	MeOH/THF	K_2CO_3	K_2CO_3
VIII	30	reflux	5	$\text{PdCl}_2(\text{PPh}_3)_2$	10	20	IPA	KOH	KOH
IX	32	reflux	5	$\text{PdCl}_2(\text{PPh}_3)_2$	10	20	IPA	KOH	KOH
X	30	reflux	5	$\text{Pd}(\text{PPh}_3)_4$	10	20	IPA	KOH	KOH
XI	30	reflux	16	$\text{Pd}(\text{PPh}_3)_4$	10	20	IPA	KOH	KOH
XII	32	reflux	3 { 16 }	$\text{PdCl}_2(\text{PPh}_3)_2$	10	20	IPA	KOH	KOH
XIII	32	reflux	3 { 72 }	$\text{Pd}(\text{PPh}_3)_4$	10	20	IPA	KOH	KOH
XIV	32	reflux	5 { 16 }	$\text{Pd}(\text{PPh}_3)_4$	10	20	IPA	KOH	KOH
XV	30	reflux	3 { 48 }	$\text{Pd}(\text{PPh}_3)_4$	10	20	IPA	KOH	KOH
XVI	30	reflux	3 { 168 }	$\text{Pd}(\text{PPh}_3)_4$	10	20	IPA	KOH	KOH
XVII	32	reflux	3 { 72 }	$\text{Pd}(\text{PPh}_3)_4$	10	20	IPA	KOH	KOH
XVIII	29	reflux	3 { 48 }	$\text{Pd}(\text{PPh}_3)_4$	10	20	IPA	KOH	KOH

[§] Co-workers have since attempted analogous reactions and have found similar results. I. R. Crossley – unpublished results.^{**} Numbers in { } indicate the time in hours for which the reaction mixture was allowed to cool to ambient temperature following reflux.

Having previously synthesised $\text{Me}_3\text{SiC}\equiv\text{C}(\text{C}_6\text{H}_4)\text{CO}_2\text{Me}$ *via* Sonogashira coupling using modified literature procedures,^{304–306} synthesis of the desired propargylidynes were attempted in similar fashion. The reaction conditions were altered such that NEt_3 was used for the dual function of solvent and base. Thus, **32** was heated to reflux in NEt_3 with $\text{I}(\text{C}_6\text{H}_4)\text{CO}_2\text{Me}$ and 20 mol% of both $[\text{PdCl}_2(\text{PPh}_3)_2]$ and CuI , with addition of TBAF after 5 min. After heating at reflux for 1 h, the reaction mixture was allowed to cool to ambient temperature over 24 h (Table 14, **V**). ^1H NMR spectroscopy showed an intractable mixture of products that included unreacted $\text{I}(\text{C}_6\text{H}_4)\text{CO}_2\text{Me}$ and retention of the SiMe_3 proton resonance after work-up, suggesting that desilylation had not been successful.

An alternative desilylation method was then implemented, with TBAF and NEt_3 replaced with a large excess of K_2CO_3 and a THF/MeOH (1:1) solvent mixture, following the work of Ren *et al.* in which both Sonogashira couplings and desilylation of a $-\text{C}\equiv\text{CSiMe}_3$ group were carried out within the coordination sphere of a metal.³⁰⁷ Additionally, as the active catalyst is a Pd^0 species, $[\text{PdCl}_2(\text{PPh}_3)_2\text{Cl}_2]$ was replaced with $\text{Pd}(\text{PPh}_3)_4$ to circumvent the need to generate a Pd^0 species *in situ*. K_2CO_3 and **30** were suspended in the solvent mixture and stirred at ambient temperature for 45 min. The mixture was then filtered into a suspension of CuI , $\text{Pd}(\text{PPh}_3)_4$ and $\text{I}(\text{C}_6\text{H}_4)\text{CO}_2\text{Me}$ in THF and heated at reflux for 3 h before allowing to cool to ambient temperature over 16 h (Table 14, **VI**). The ^1H NMR spectrum of the crude product indicated an intractable mixture of products, which included unreacted $\text{I}(\text{C}_6\text{H}_4)\text{CO}_2\text{Me}$; aqueous work up failed to isolate one product. The reaction was repeated, with all reagents suspended together in THF/MeOH; the quantity of $\text{Pd}(\text{PPh}_3)_4$ was also reduced to 10 mol% (**VII**). The mixture was heated to reflux for 3 h and allowed to cool to ambient temperature for 16 h – similar results were obtained. The presence of both $\text{I}(\text{C}_6\text{H}_4)\text{CO}_2\text{Me}$ and a strong signal assigned to the SiMe_3 protons of **32** in the crude product suggested that desilylation had again been unsuccessful.

An alternative desilylation method was implemented by replacing K_2CO_3 with KOH and the solvent system with propan-2-ol. The reaction was repeated with $[\text{TpMo}(\text{CO})_2(\equiv\text{CC}\equiv\text{CSiMe}_3)]$ (**30**), $\text{I}(\text{C}_6\text{H}_4)\text{CO}_2\text{Me}$, CuI (10 mol%) and $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$ (20 mol%) (Table 14, **VIII**); the mixture was heated at reflux for 5 h. Interestingly, the SiMe_3 protons were no longer visible in a ^1H NMR spectrum of the crude product, whilst the Tp-H^3 protons were observed to have shifted to δ_{H} 6.34 and 6.18, integrating *ca.* 1:2, respectively. This is in contrast to the starting material, where the Tp-H^3 resonances are observed at δ_{H} 6.35 and 6.14 and integrated 2:1, respectively. Despite this promising result and loss of the SiMe_3 proton resonance, it appeared that the methyl ester functionality had been lost. Two multiplet resonances at δ_{H} 7.69 and 7.66 seemed to indicate retention of the phenyl spacer; however, with multiple resonances in the aryl region due to decomposition of the Pd catalyst, assigning such peaks was somewhat problematic. Similar

results were obtained with the Tp* analogue (**IX**). Column chromatography failed to isolate one product, though a change in the ratio of the two Tp-H³ proton resonances to 1:4 was observed.

Upon repeating the reaction with the Pd⁰ complex [Pd(PPh₃)₄] (Table 14, **X**), Tp-H³ resonances were observed at δ_{H} 6.17 and 6.08; contrary to the previous experiment, the resonances integrated 2:1, respectively. Upon aqueous work up, the two Tp-H³ resonances integrated 1:1. In each case, the change in integration of the Tp resonances suggests that there is more than one Tp-containing product and that Tp is no longer ligated to the metal centre, as all H³ protons are in the same chemical environment. The reaction was repeated with the reaction mixture heated to reflux for 16 h (**XI**), before being passed through an alumina column with a DCM/hexane (5:1) eluent. Whilst a resonance consistent with a Tp-H³ proton was distinguishable at δ_{H} 6.07, no other resonances of significance were observed.

Reaction conditions **VIII–X** (Table 14) had proven most successful, with the common factor being the extended reflux time. Combining this information with the Sonogashira coupling conditions, which were proven successful for the synthesis of Me₃SiC≡C(C₆H₄)CO₂Me (*vide supra*), reaction conditions **XII–XVII** were evaluated. This involved heating the mixture to reflux for an extended period and allowing the reaction mixture to cool to ambient temperature for at least 16 h. While this had been previously attempted under reaction conditions **V–VII**, less successful solvent/base combinations had been used in those cases. Initially, the Pd^{II} pro-catalyst [PdCl₂(PPh₃)₂] was used (**XII**) with resonances in the ¹H NMR spectrum of the crude product observed at δ_{H} 5.82 and 5.62, integrating 2:1 respectively and shifted slightly from those of the starting material (δ_{H} 5.84, 5.69). While these data seemed promising indicators for retention of the Tp* ligand in a slightly different chemical environment, ¹¹B{¹H} NMR spectroscopy showed the presence of two boron-containing product at δ_{B} -9.9 and -16.8.

Repeating the reaction using [Pd(PPh₃)₄] led to varying levels of success. Reaction conditions **XIII–XVII** were unsuccessful, with **XIII–XVI** showing the presence of protons from the SiMe₃ fragment in ¹H NMR spectra of the crude reaction mixture. While these protons were lost following reaction conditions **XVII**, multiple Tp*-containing products were apparent. Given the similar nature of reactions **XIII–XVII**, it is difficult to speculate as to why reaction conditions **XVII** appeared to lead to desilylation while the other reactions did not.

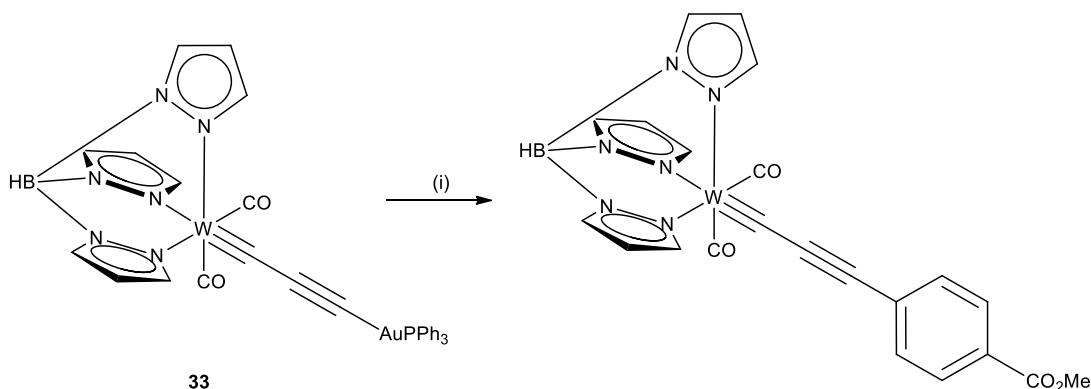
The reaction was repeated under conditions **XVIII** with the tungsten analogue [TpW(CO)₂(≡CC≡CSiMe₃)] (**29**). Not only did desilylation occur, but two resonances consistent with Tp-H³ protons were observed in the ¹H NMR spectrum, with the expected relative integration, at δ_{H} 6.20 and 6.13. Additionally, a broad resonance at δ_{H} 3.96 was observed,

integrating to 3, consistent with the Me protons of the methyl ester functionality. However, other products were also observed in the ^1H NMR spectrum and resonances in the aryl region were difficult to assign due to degradation products of the catalyst. Purification of the product was attempted, but was met with limited success; therefore, synthesis of the desired product could not be confirmed conclusively.

3.2.2.2 Propargylidynes via Au Coupling Reactions

In view of the difficulties encountered with *in situ* desilylation, the methodology of Antonova *et al.*²⁷⁰ was considered wherein Au(PPh₃)-terminated complexes were coupled with a series of halogenated sp- and sp²- carbon compounds (*vide supra*) under Sonogashira conditions. Initial attempts to synthesise [TpW(CO)₂(≡CC≡CAu(PPh₃))] (**33**) following literature procedures outlined by Bruce *et al.*²⁶³ met with limited success. However, **33** was successfully synthesised *via* procedures outlined by Dewhurst *et al.*,²⁷¹ *viz.* addition of TBAF to a mixture of **29** and [AuCl(PPh₃)] in DCM.

The synthesis of [TpW(CO)₂(≡CC≡C(C₆H₄)CO₂Me)] was attempted by reaction of **33** with I(C₆H₄)CO₂Me and catalytic amounts of Pd(PPh₃)₄ and CuI,^{263,274} with the reaction mixture heated at reflux in THF for 4 h. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum indicated loss of the PPh₃ moiety, with several small, broad resonances between δ_{P} 27.1 and 19.3, presumably corresponding to degradation products of the Au fragment. The ^1H NMR spectrum showed promising results, with resonances at δ_{H} 6.31 and 6.19, corresponding to the Tp-H³ protons, having shifted from those seen for **33** (δ_{H} 6.25 and 6.14, respectively). In addition, a resonance at δ_{H} 3.88 was observed, integrating to 3 protons with respect to the Tp ligand. This also represents a shift from the starting material with the CH₃ protons of I(C₆H₄)CO₂Me observed at δ_{H} 3.91. Assigning the phenyl protons was again challenging due to degradation products of the Au(PPh₃) fragment, with multiple resonances observed in the aryl region. Attempts to purify and isolate any one product proved unsuccessful. With only small shifts in frequency of the Tp and Me protons in the ^1H NMR spectrum of the product compared to reagents, the success of the reaction was debateable. Discrepancy exists between these data and those of the more promising products resulting from reactions summarised in Table 14. The Tp resonances would be expected to have the same 2:1 distribution of the Tp-H³ protons for all products, which was not the case.



Scheme 53: Coupling reaction to synthesise $[\text{TpW}(\text{CO})_2(\equiv\text{CC}\equiv\text{C}(\text{C}_6\text{H}_4)\text{CO}_2\text{Me})]$. *Reagents and Conditions:* (i) $\text{I}(\text{C}_6\text{H}_4)\text{CO}_2\text{Me}$, $\text{Pd}(\text{PPh}_3)_4$, CuI , THF.

3.3 CONCLUDING REMARKS

Attempts to synthesise the metal–alkynyl complexes $[\text{RuH}(\text{CO})_2(\text{PPh}_3)_2(\text{C}\equiv\text{CCO}_2\text{H})]$ and $[\text{RuH}(\text{CO})_2(\text{PPh}_3)_2(\text{C}\equiv\text{CCH}_2\text{Cl})]$ from Roper's complex were met with limited success, however, the novel allenylidene complex $[\text{RuCl}(\text{CO})_2(\text{PPh}_3)_2(\text{CH}=\text{C}=\text{CH}_2)]$ was furnished in admixture with the previously reported dihydride $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$. Additionally, a series of vinylidene and alkynyl complexes were successfully synthesised from $[\text{RuCl}(\text{dppe})_2][\text{OTf}]$, including novel examples bearing CO_2Me , CO_2Et , Ph and CO_2Et ester termini. Furthermore, a series of related hydrido complexes were furnished leading to the conclusion that the vinylidene/alkynyl tautomerism reactions occurring in this case are catalytic in nature, with stoichiometric quantities of KO^tBu leading to the generation of metal–hydrides. While attempts to install a phosphaalkenic terminus onto these metal–alkynyls was met with limited success, a novel vinylidene complex was furnished with the introduction of a $\text{P}(\text{TMS})_n$ ligand, though the exact nature of this compound could not be conclusively determined.

Difficulties in the preparation of the propargylidyne complexes $[\text{M}(\text{C}\equiv\text{CC}\equiv\text{CO}_2\text{Me})\{\text{OC}(\text{O})\text{CF}_3\}(\text{CO})_2(\text{tmeda})]$ ($\text{M} = \text{W}, \text{Mo}$) led to the pursuit of related compounds of the type $[\text{Tp}'\text{M}(\equiv\text{CC}\equiv\text{CCO}_2\text{Me})(\text{CO})_2]$, however, retention of the desired ester termini proved problematic. As such, compounds of the type $[\text{Tp}'\text{M}(\equiv\text{CC}\equiv\text{CC}_6\text{H}_4\text{CO}_2\text{Me})(\text{CO})_2]$ were instead pursued *via* coupling reactions. This initially involved Sonogashira-type coupling reactions between the known compounds $[\text{Tp}'\text{M}(\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{CO})_2]$ and the iodobenzoate $\text{IC}_6\text{H}_4\text{CO}_2\text{Me}$ in the presence of CuI and $\text{Pd}^0/\text{Pd}^{\text{II}}$ compounds in catalytic quantities. Difficulties in assigning resonances in the ^1H NMR spectra of the resultant products were considered a

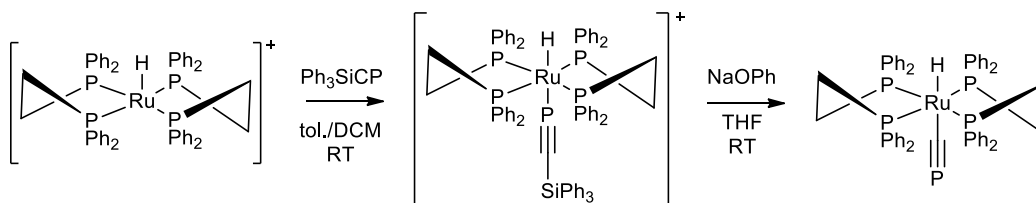
result of degradation products of the Pd-aryl catalyst in combination with unsuccessful desilylation of the $-\text{C}\equiv\text{CSiMe}_3$ terminus in many cases. As such, coupling reactions between the Au terminated propargylidyne $[\text{TpW}(\equiv\text{CC}\equiv\text{CAuPPh}_3)(\text{CO})_2]$ and $\text{IC}_6\text{H}_4\text{CO}_2\text{Me}$ were carried out. Despite some promising results from both types of coupling reaction, no one product could be unambiguously identified from the data obtained.

CHAPTER 4: THE SYNTHESIS AND STRUCTURE OF RUTHENIUM CYAPHIDE COMPLEXES

4.1 INTRODUCTION

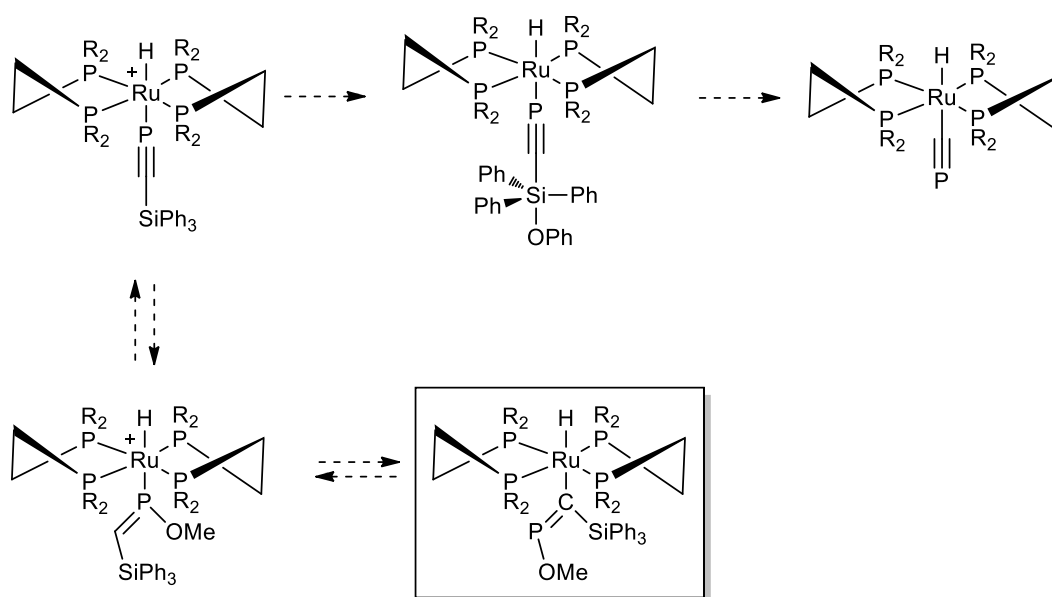
The cyaphide ligand, $-\text{C}\equiv\text{P}$, has been of particular interest in the field of low coordinate phosphorus chemistry due to the diverse utility of its nitrogen analogue cyanide, $-\text{C}\equiv\text{N}$ and the established similarities between $\text{C}\equiv\text{P}$ and $\text{C}\equiv\text{C}$ bonds; however, little is known about this elusive ligand due to difficulties associated with its synthesis. Prior to 2006, synthesis of a cyaphide compound had merely been alluded to. While Angelici and co-workers¹⁷⁹ were unable to isolate a terminal cyaphide, they inferred its synthesis by demonstrating subsequent η^2 -coordination of the cyaphide fragment to a second metal complex, and also went on to coordinate to a third metal centre through the phosphorus lone pair.¹⁸¹ The transient terminal cyaphide species was characterised by ^{31}P NMR spectroscopy alone, with resonances observed at δ_{P} 68.0 and δ_{P} 7.3 with mutual coupling ($^3J_{\text{PP}} = 9.2$ Hz). Computational studies were later carried out to determine the nature of the cyaphide species. A theoretical $\text{C}\equiv\text{P}$ bond length of 1.566 Å was calculated with a vibration frequency of 1383 cm^{-1} predicted.¹⁶⁸

The first example of an isolable terminal cyaphide complex was synthesised by Grützmacher¹⁷⁷ in 2006 from the η^1 -coordinated phosphalkyne complex $[\text{RuH}(\text{dppe})_2(\eta^1\text{-P}\equiv\text{CSiPh}_3)][\text{OTf}]$ (Chapter 1, Section 1.3.2) upon addition of NaOPh , furnishing $[\text{RuH}(\text{dppe})_2(\text{C}\equiv\text{P})]$ (Scheme 54). A $\text{C}\equiv\text{P}$ phosphorus resonance at δ_{P} 165.0 was observed, having shifted downfield from the phosphalkyne precursor. This differs significantly from that of Angelici's unstable cyaphide, however, given the wide ranging shifts exhibited by phosphorus centres of free phosphalkynes, this is not necessarily unexpected.¹⁷⁶ The cyaphide complex $[\text{RuH}(\text{dppe})_2(\text{C}\equiv\text{P})]$ was found to have a carbon resonance at δ_{C} 287.1, also demonstrating a significant downfield shift from the parent phosphalkyne, reflecting the deshielding of the $\text{C}\equiv\text{P}$ carbon centre. The structure was confirmed by X-ray diffraction data, demonstrating a $\text{C}\equiv\text{P}$ bond length of 1.573(2) Å – the longest uncoordinated $\text{C}\equiv\text{P}$ bond reported to date. It was speculated that this was a result of back-bonding from the metal into the π^* orbitals of the $\text{C}\equiv\text{P}$ moiety.



Scheme 54: Synthesis of the first stable cyaphide compound.

An intermediate species was also reportedly observed during formation of $[\text{RuH}(\text{dppe})_2(\text{C}\equiv\text{P})]$ (Scheme 55), exhibiting a quintet and a doublet resonance with mutual spin–spin coupling in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (δ_{P} 309.5 and 62.7 respectively; $J_{\text{PP}} = 27$ Hz) and thought to be a C-metallated phosphalkene; its presence was seen to diminish with the emergence of the cyaphide product. A mechanism for the formation of the cyaphide complex was thus proposed whereby attack at phosphorus by ^-OPh occurs initially, followed by rearrangement to the C-metallated phosphalkene *via* an η^2 -bound phosphalkyne transition state. Elimination of the silyl ether PhOSiPh_3 would then occur *via* a second transition state in which ^-OPh interacts with both phosphorus and silicon. However, a very high energy barrier to access this transition state was calculated using DFT studies. An alternative mechanism was proposed in which ^-OPh attacks at silicon, followed by η^2 -coordination of the phosphalkyne and subsequent loss of the silylether. Grützmacher hypothesised that attack at phosphorus is kinetically favoured but reversible and therefore, both pathways are occurring simultaneously. Attack at silicon with formation of the five-coordinate silyl transition state is thermodynamically favoured and ultimately forms the cyaphide ligated ruthenium complex.



Scheme 55: Proposed mechanism of cyaphide formation ($\text{R} = \text{Ph}$) upon addition of NaOPh , with formation of an intermediate species observed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy.³⁰⁸

Since the publication of this seminal work, there has been no further work on the cyaphide ligand. Russell *et al.*¹⁷⁴ were recently able to synthesise the bis(η^1 -phosphaalkyne) complex $[\text{Mo}(\text{dppe})_2(\text{P}\equiv\text{CSiMe}_3)_2]$, with subsequent addition of TBAT (tetrabutylammonium

triphenyldifluorosilane) furnishing a unique compound with a phosphorus resonance at δ_P 65.5 assigned to the dppe ligands and two further resonances in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum observed at δ_P 197.8 and 183.0. This was considered indicative of two inequivalent $\text{C}\equiv\text{P}$ moieties and the compound assigned as the mixed η^1 -phosphaalkyne–cyaphide complex $[\text{Mo}(\text{dppe})_2(\text{P}\equiv\text{CSiMe}_3)(\text{C}\equiv\text{P})]^-$. However, this compound was only observed *in situ* and could not be unambiguously identified from the available data.

With so few examples of cyaphide-containing compounds demonstrated thus far, their properties remain largely unexplored with regard to structure, reactivity and electronics. Incorporation of this ligand into conjugated organometallic complexes holds promise with respect to molecular wire design and synthesis. Having previously synthesised a range of ruthenium alkynyl compounds of the type $[\text{RuCl}(\text{dppe})_2(\text{C}\equiv\text{CR})]^+$, the possibility of combining the two systems, alkynyl and cyaphide, in a *trans*-disposition was explored. The synthesis of such compounds was pursued and their subsequent reactivity is described herein.

4.2 SYNTHESIS AND STRUCTURE OF RUTHENIUM η^1 -PHOSPHAALKYNE COMPLEXES

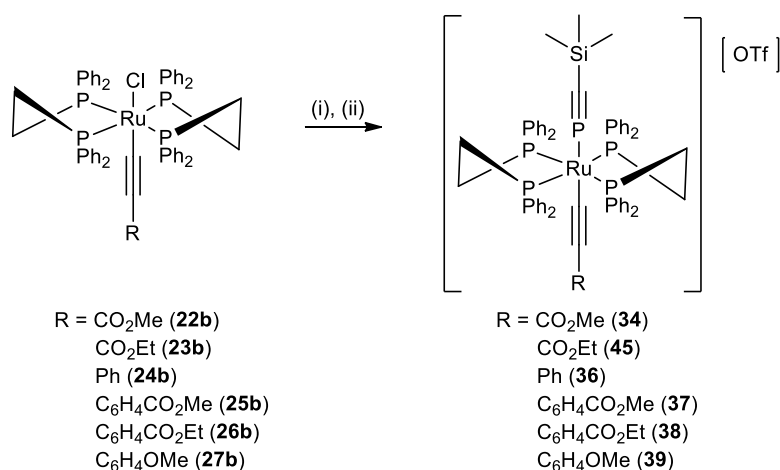
$[\text{Ru}(\text{dppe})_2(\text{C}\equiv\text{CR})(\eta^1\text{-P}\equiv\text{CSiMe}_3)]$

4.1.1 SYNTHESIS AND CHARACTERISATION

Compounds of the type $[\text{RuCl}(\text{dppe})_2(\text{C}\equiv\text{CR})]$ (**22–27(b)**) were dissolved in DCM with AgOTf and stirred under ambient conditions; after 5 min a solution of $\text{P}\equiv\text{CSiMe}_3$ in toluene was added and the mixture stirred for 1 h. Subsequent filtration and removal of solvent under reduced pressure afforded the complexes $[\text{Ru}(\text{dppe})_2(\text{C}\equiv\text{CR})(\text{P}\equiv\text{CSiMe}_3)][\text{OTf}]$ (**34–39**; Scheme 56) as orange/red solids. Complexes **34–39** were identified initially on the basis of $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, each exhibiting quintet and doublet resonances at approximately δ_P 110 and 42, respectively, with mutual $^2J_{\text{PP}}$ couplings of *ca.* 34 Hz (Table 16). Singlet resonances in the ^1H NMR spectra assigned to the SiMe_3 methyl protons (*ca.* δ_H –10.0) correlate to characteristic doublet resonances in the corresponding $^{13}\text{C}\{^1\text{H}\}$ NMR spectra at around δ_C 190 ($^1J_{\text{CP}}$ ~90 Hz), assigned by $^{13}\text{C}/^1\text{H}$ -HMBC; these are attributable to the phosphaalkynic carbon atoms, consistent with coordination of the $\text{P}\equiv\text{CSiMe}_3$ fragment in each case. These data resemble those of Grützmacher's η^1 -phosphaalkyne $[\text{RuH}(\text{dppe})_2(\text{P}\equiv\text{CSiPh}_3)][\text{OTf}]$ (δ_P 143.8, 60.1; $^2J_{\text{PP}}$ 27.3 Hz. δ_C 175.1; $^1J_{\text{CP}}$ 71.4 Hz) with somewhat more shielded phosphorus resonances observed for compounds **34–39**. HSQC and HMBC experiments were carried out to aid spectral assignment and bulk purity was confirmed by elemental analysis. Infrared spectroscopy of compounds **34–**

39 exhibit strong bands between 1248–1269 cm^{-1} , assigned to the $\text{P}\equiv\text{C}$ stretch; such stretching frequencies are typical for $\text{P}\equiv\text{C}$ stretches in η^1 -coordinated phosphalkyne complexes.^{154,172,174–177,309–313}

Complexes **34/35** and **36–39** show distinctive differences in their $^{13}\text{C}\{^1\text{H}\}$ NMR spectra with regard to the alkynyl ligands. Complexes bearing an aryl ring (**36–39**) demonstrate more shielded carbon resonances for those carbon atoms in close proximity to the phenyl spacer (*i.e.* the β -carbon and $\text{C}=\text{O}$ carbon) than those observed for complexes **34/35**. In addition, the α -carbon of compounds **34/35** demonstrate more deshielded resonances than those of **36–39**. A similar trend is observed for the $\text{P}\equiv\text{CSiMe}_3$ ligand, with **34/35** demonstrating a more deshielded phosphorus centre and more shielded carbon centre with respect to compounds **36–39**. IR spectroscopic data show little difference in the $\text{C}\equiv\text{P}$, $\text{C}\equiv\text{C}$ and $\text{C}=\text{O}$ stretching frequencies of the six complexes.



Scheme 56: Synthesis of complexes **34–39**. *Reagents and Conditions:* (i) AgOTf , DCM , 5 min, r.t.; (ii) $\text{TMSC}\equiv\text{P}$, toluene, 1 h, r.t.

4.2.2 STRUCTURAL PROPERTIES OF **34**

Identity of **34** was further supported by X-ray diffraction studies, with crystals obtained by slow cooling of a saturated solution of **34** in CDCl_3 (Figure 29). A $\text{C}\equiv\text{C}$ bond length of 1.151(14) Å lies within the limits of statistical comparability to that of the parent chloride, **22b** (1.136(5) Å), alongside a characteristic $\text{P}\equiv\text{C}$ phosphalkynic bond length of 1.527(11) Å.¹¹³ A $\text{P}-\text{C}-\text{Si}$ bond angle of $178.3(8)^\circ$ for **34** demonstrates almost complete linearity, while a $\text{Ru}-\text{P}-\text{C}$ bond angle of $175.7(4)^\circ$ deviates slightly further from a linear geometry (*vide infra*). These data are

comparable to those of $[\text{RuH}(\text{dppe})_2(\text{P}\equiv\text{CSiPh}_3)][\text{OTf}]$ ($d_{\text{PC}} = 1.530(3) \text{ \AA}$; $\text{P}-\text{C}-\text{Si}$ $165.5(2)^\circ$; $\text{Ru}-\text{P}-\text{C}$ 174.8°) and $[\text{Mo}(\text{dppe})_2(\text{P}\equiv\text{CSiMe}_3)_2]$ ($d_{\text{PC}} = 1.540(2) \text{ \AA}$; $\text{P}-\text{C}-\text{Si}$ $179.59(15)^\circ$; $\text{Ru}-\text{P}-\text{C}$ $178.58/176.30^\circ$).

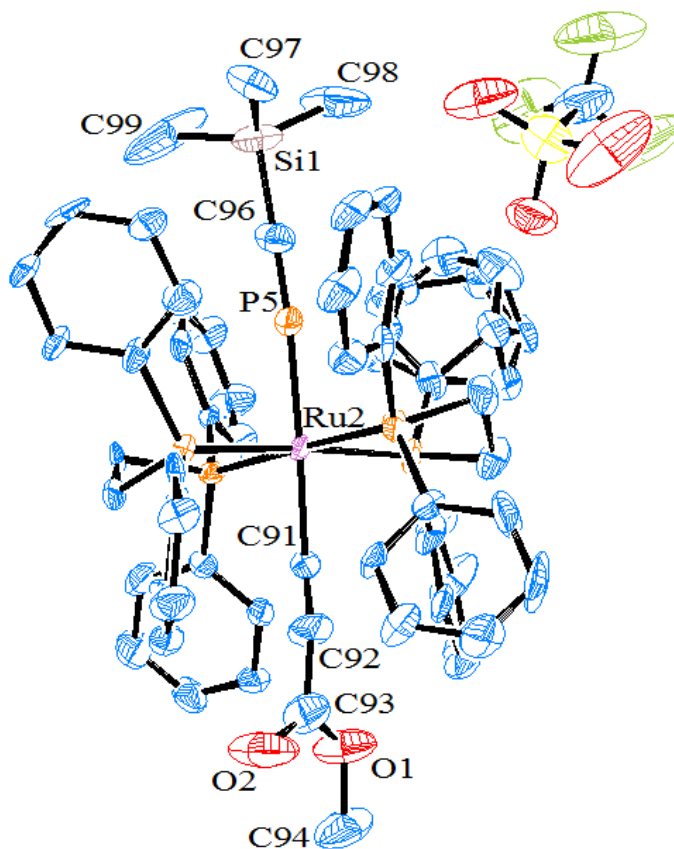


Figure 29: Molecular structure for **34**. H atoms omitted for clarity. 50% thermal ellipsoids.

Table 15: Selected Bond Lengths (\AA) and Angles ($^\circ$) for **34**

	X-Ray
$\text{Ru}(2)-\text{C}(91)$	$2.083(10)$
$\text{Ru}(2)-\text{P}(5)$	$2.274(3)$
$\text{P}(5)-\text{C}(96)$	$1.527(11)$
$\text{C}(96)-\text{Si}(1)$	$1.859(11)$
$\text{C}(91)-\text{C}(92)$	$1.151(14)$
$\text{P}(5)-\text{C}(96)-\text{Si}(1)$	$178.3(8)$
$\text{C}(96)-\text{P}(5)-\text{Ru}(2)$	$175.7(4)$

Table 16: Selected $^{31}\text{P}\{^1\text{H}\}$ (161.7 MHz) and $^{13}\text{C}\{^1\text{H}\}$ (100.5 MHz) NMR shifts (ppm) and IR stretches (cm^{-1}) for complexes of the type $[\text{Ru}(\text{dppe})_2(\text{TMSC}\equiv\text{P})(\text{C}\equiv\text{CR})][\text{OTf}]$ (in CDCl_3) and $[\text{Ru}(\text{dppe})_2(\text{C}\equiv\text{P})(\text{C}\equiv\text{CR})]$ (in CD_2Cl_2)^{††}

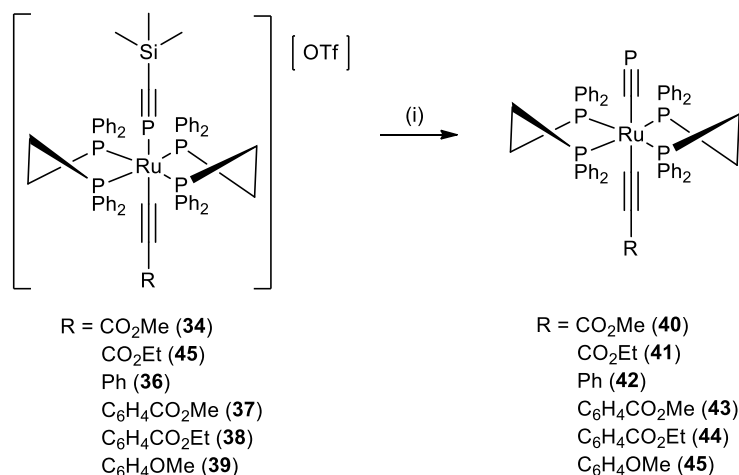
R	Compound No.	δ_{P}		δ_{C}			ν			
		$\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2$ ($^2J_{\text{PP}}$, Hz)	$\text{C}\equiv\text{P}$ ($^2J_{\text{PP}}$, Hz)	$\text{C}\equiv\text{P}$ ($^1J_{\text{CP}}$, Hz)	$\text{C}_\alpha\equiv\text{C}_\beta$	$\text{C}_\alpha\equiv\text{C}_\beta$	$\text{C}=\text{O}$	$\text{C}\equiv\text{P}$	$\text{C}\equiv\text{C}$	$\text{C}=\text{O}$
CO_2Me	34	41.2 (35.0)	108.4 (35.0)	192.6 (89.9)	120.8	108.8	152.7	1265	2098	1680
CO_2Et	35	41.2 (33.6)	108.6 (33.6)	192.4 (88.7)	119.8	109.0	152.4	1265	2087	1672
Ph	36	42.4 (33.1)	112.5 (33.1)	188.6 (88.0)	108.5	116.2	N/A	1265	2024	N/A
$\text{C}_6\text{H}_4\text{CO}_2\text{Me}$	37	41.8 (33.0)	111.0 (33.0)	190.2	108.8	116.0	167.0	1248	2066	—
$\text{C}_6\text{H}_4\text{CO}_2\text{Et}$	38	41.6 (33.2)	111.1 (33.2)	190.3	—	116.0	166.5	1269	2087	1706
$\text{C}_6\text{H}_4\text{OMe}$	39	42.2 (31.9)	113.1 (31.9)	188.2 (86.8)	104.7	115.9	N/A	1265	2040	N/A
R		$\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2$ ($^3J_{\text{PP}}$, Hz)	$\text{C}\equiv\text{P}$	$\text{C}\equiv\text{P}$	$\text{C}_\alpha\equiv\text{C}_\beta$	$\text{C}_\alpha\equiv\text{C}_\beta$	$\text{C}=\text{O}$	$\text{C}\equiv\text{P}$	$\text{C}\equiv\text{C}$	$\text{C}=\text{O}$
CO_2Me	40	49.7 (3.8)	168.5	279.1	143.8	112.4	153.0	1253	2036	1660
CO_2Et	41	49.8 (4.8)	168.5	278.7	141.8	112.0	152.0	1253	2044	1656
Ph	42	50.9 (4.0)	160.6	281.5	—	119.8	N/A	1239	1901	N/A
$\text{C}_6\text{H}_4\text{CO}_2\text{Me}$	43	50.7 (2.5)	165.4	280.7	140.1	120.3	167.7	1269	2054	1710
$\text{C}_6\text{H}_4\text{CO}_2\text{Et}$	44	50.6 (2.7)	165.3	280.8	139.8	120.3	167.2	1246	2054	1703
$\text{C}_6\text{H}_4\text{OMe}$	45	52.7 (3.9)	161.5	282.0	—	118.9	N/A	1261	2032	N/A

^{††} Values marked with ‘—’ could not be assigned.

4.2 SYNTHESIS OF RUTHENIUM CYAPHIDES $[\text{Ru}(\text{dppe})_2(\text{C}\equiv\text{CR})(\text{C}\equiv\text{P})]$

4.2.1 SYNTHESIS AND CHARACTERISATION

Treatment of complex **34** with 1 equivalent of KO^tBu in THF led to formation of the desired cyaphide–alkynyl compound **40** (Scheme 57) after constant stirring under ambient conditions for 1 h. A high frequency shift was observed for the $\text{P}\equiv\text{C}$ and dppe phosphorus resonances to δ_{p} 161.5 and 52.7, which appear as a broad multiplet and doublet, respectively. The latter exhibited a spin–spin coupling of 3.8 Hz, markedly different from the $^2J_{\text{PP}}$ -coupling of 35.0 Hz observed for **34** (Table 16). In addition, a significant shift downfield of the $\text{P}\equiv\text{C}$ carbon centre of *ca.* 86 ppm to δ_{C} 279.1 was observed. These data are comparable to those of Grützmacher's cyaphide complex (δ_{p} 165.0, 65.2; δ_{C} 287.1). Cyaphide complexes **41–45** were prepared similarly from complexes **35–39**, respectively; comparable spectroscopic data are observed for all analogues (Table 16).



Scheme 57: Synthesis of compounds **40–45**. *Reagents and Conditions:* (i) KO^tBu , THF, 1 h, r.t.

Complexes **40–45** exhibited strong stretches in their respective IR spectra between 1239–1269 cm^{-1} (Table 16). For compound **40**, this was observed at 1253 cm^{-1} , with Raman spectroscopy showing an intense band at 1271 cm^{-1} . These data compare well with those calculated by DFT studies, which suggest bands at 1262 cm^{-1} in both the Raman and IR spectra for **40** (B3LYP/6-31G** for H,C,O,P; LANL2DZ for Ru).^{‡‡} Furthermore, these data are comparable to those observed experimentally for $[\text{RuH}(\text{dppe})(\text{C}\equiv\text{P})]$ (1229 cm^{-1}). Interestingly, complexes **43** and **44** exhibit C=O stretches at a notably higher frequency than those of **40** and **41**, suggesting a

^{‡‡} IR stretches calculated by DFT studies were scaled with a scaling factor of 0.9806.³²¹

weaker P≡C bond in the latter compounds.

Positive ion ESI mass spectrometry of **40** reveals major peaks at m/z 983, 1009 and 1097; the parent compound was observed as a very minor component of the spectrum. Interestingly, m/z 983 is consistent with an MH^+-Me fragment, suggesting loss of CH_3 during ionisation; compounds **41** and **43–44** also demonstrated loss of a CH_3 group. Elemental analysis of the cyaphide-containing complexes met with some difficulty due to the persistence of KOTf in the product, the presence of which was confirmed by ^{19}F NMR spectroscopy (δ_F -78.9). Re-dissolving **40** in CH_2Cl_2 and subsequent filtration of the mixture led to removal of a cream coloured solid from the bulk material, thought to be KOTf, with elemental analysis results significantly improved as a result, however, complete removal was not achieved.

Interestingly, while Grützmacher reports reaction times of approximately 14 h for the synthesis of $[RuH(dppe)_2(C\equiv P)]$, reaction times of <1 h were routinely observed for the formation of complexes **40–45**.³⁰⁸ Additionally, and in contrast to the synthesis of Grützmacher's terminal cyaphide complexes (*vide supra*), an intermediate was not observed in the formation of complexes **40–45**, even when employing NaOPh as a base. Neither was an intermediate observed during an *in situ* $^{31}P\{^1H\}$ NMR spectroscopy study at -78 °C. This may be due to the smaller silyl group, $SiMe_3$, causing less steric hinderence compared to $SiPh_3$, thereby facilitating nucleophilic attack. Additionally, the electron-withdrawing nature of the " $Ru(C\equiv CCO_2Me)$ " fragment may result in electron density being drawn towards the metal centre. This would render the silicon centre more electropositive, which would facilitate nucleophilic attack at silicon, to the extent where this might happen preferentially and by-pass any phosphalkenyl intermediate. This is supported by NMR spectroscopic data; while ^{29}Si data are not available for $[RuH(dppe)_2(P\equiv CSiPh_3)][OTf]$, a shift of δ_{Si} -12.3 for **34** is somewhat more deshielded than that of the free ligand ($Me_3SiC\equiv P$: δ_{Si} -16.1). Furthermore, the $C\equiv P$ ligand exhibits a carbon resonance at δ_C 192.6 and phosphorus resonance at δ_P 108.4, which differ to those reported for $[RuH(dppe)_2(P\equiv CSiPh_3)][OTf]$ (δ_C 175.1; δ_P 143.8) due to the shift in electron density towards the " $RuC\equiv CCO_2Me$ " fragment. DFT calculations give further credence to this hypothesis. An optimised structure for **34** (B3LYP/6-31G** for H,C,O,P; LANL2DZ for Ru) shows relative Mulliken charges of 0.649 and 0.098 associated with the Si and P centres respectively, clearly proving silicon to be far more electropositive than phosphorus in the $Me_3SiC\equiv P$ fragment.

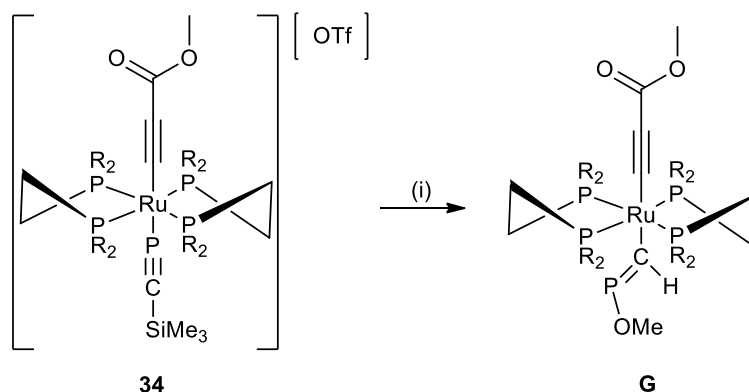
Upon addition of a methanolic solution of KO^tBu to a solution of **34** in DCM, a new product was observed (complex **G**). Resonances in the $^{31}P\{^1H\}$ NMR spectrum at δ_P 298.3 (qnt, $J_{PP} = 7.9$ Hz) and δ_P 52.1 (d, $J_{PP} = 7.9$ Hz) were noted to be very similar to those of Grützmacher's intermediate complex. Intuitively, it might seem that the presence of methoxide ions in this

reaction led to an analogous phosphalkenyl compound having been formed; however, with the loss of the SiMe₃ group implied by the absence of methyl protons in the ¹H NMR spectrum, it would seem that this is not the case. Additionally, a resonance is observed at δ_{H} 8.51 (dqnt, J_{HP} = 20.8, 6.8 Hz), while the relative shift may be consistent with a phosphalkenic proton,^{155,164} it is far more deshielded than that observed for Grützmacher's intermediate (δ_{H} 2.91; d, $^2J_{\text{HP}}$ = 28 Hz) and exhibits further multiplicity. Furthermore, this highly deshielded proton resonance did not display any interaction with a carbon resonance in either HSQC or HMBC experiments. However, the relative shift of the phosphorus/hydrogen resonances, combined with a doublet of multiplets in the ³¹C{¹H} NMR spectrum at δ_{C} 175.1, would imply the formation of a phosphalkenyl-type structure.

The "C \equiv CCO₂Me" fragment was retained in the product, with a singlet resonance in the ¹H NMR spectrum assigned to the methyl protons (δ_{H} 3.58), with the ¹³C{¹H} spectrum displaying broad C \equiv C resonances at δ_{C} 146.6 and 112.5. Additionally, strong bands in the IR spectrum at 2044 and 1660 cm⁻¹ can be assigned to C \equiv C and C=O stretches, respectively.

Broad multiplet resonances were observed in the ¹H NMR spectrum and assigned to the dppe protons. Additionally, a doublet was observed at δ_{H} 2.67 integrating to *ca.* 3 protons, with a J_{HP} interaction of 6.69 Hz, consistent with a 3-bond H–P separation. This resonance demonstrated a correlation to a carbon resonance at δ_{C} 51.25 (d, $^2J_{\text{CP}}$ = 7.4 Hz) in a ¹³C/¹H HSQC experiment, lying in close proximity to the carbon atom of the ester OMe fragment (δ_{C} 51.20). It could therefore be inferred from this data that a P–O–CH₃ fragment may be present. The product was contaminated with a small amount of [RuH(dppe)₂(C \equiv CCO₂Me)] (**22c**) (*ca.* 4%). Positive-ion ESI-MS of the compound showed one major peak at *m/z* 981, consistent with the presence of **22c**. Only trace quantities of other fragments could be seen in the spectrum.

Based on the above data, complex **G** was tentatively assigned as [Ru(dppe)₂(C \equiv CCO₂Me)(P(OMe)CH)][OTf] (Scheme 58). Elemental analysis of the product was carried out to confirm the gross composition and was consistent with a compound of molecular formula C₅₉H₅₂O₆P₅F₃SRu. However, crystals of complex **G** suitable for X-ray diffraction studies have not been forthcoming; as such, the nature of this compound cannot be definitively concluded.



Scheme 58: Proposed structure of compound **G** ($R = \text{Ph}$), formed upon addition of KO^tBu in MeOH to **34**. *Reagents and Conditions:* (i) KO^tBu , MeOH, DCM, 1h, r.t.

4.2.2 ELECTRONIC AND STRUCTURAL PROPERTIES OF COMPLEXES **40–45**

DFT calculations of **40** were able to identify some of the electronic features of the cyaphide–alkynyl complexes (B3LYP/6-31G** for H,C,P,O; LANL2DZ for Ru) (Figure 30). The HOMO and HOMO-1 are heavily associated with the orthogonal π -orbitals of the $\text{C}\equiv\text{P}$ bond, which account for *ca.* 50% of the orbital contribution. The phosphorus lone pair lies at HOMO-6, which is 1.57 eV lower in energy than the HOMO; however, the major contribution to this molecular orbital comes from the $\text{C}\equiv\text{C}$ π -system (39% contribution). These data have implications for the further reactivity of this complex, suggesting that η^2 -coordination of the $\text{C}\equiv\text{P}$ bond would be more favourable than η^1 -coordination, which is in agreement with results obtained by Angelici and co-workers, wherein the cyaphide ligand could only be isolated when demonstrating η^2 -coordination to a second metal centre (*vide infra*). However, steric hinderance as a result of the dppe ligands might prevent such reactivity. DFT studies were also able to shed some light on the structural features of **40**, with bond angles for the cyaphide and alkynyl ligands found to deviate slightly from linearity ($\text{Ru}-\text{C}-\text{P}$ 177.32° ; $\text{Ru}-\text{C}-\text{C} = 177.73^\circ$); a $\text{C}\equiv\text{P}$ bond length of 1.583 Å (Table 17) was also calculated. These data resemble closely those of the only cyaphide ligand previously reported, $[\text{RuH}(\text{dppe})_2(\text{C}\equiv\text{P})]$ ($\text{Ru}-\text{C}-\text{P}$ $177.9(1)^\circ$; $d_{\text{CP}} = 1.573(2)$ Å). The ‘bending’ of the $\text{Ru}-\text{C}-\text{P}$ moiety is likely a result of the steric bulk arising from the dppe ligands. Indeed, on repeating the optimisation of **40** and replacing the dppe phenyl rings with methyl groups, the $\text{Ru}-\text{C}-\text{P}$ bond angle is calculated as being almost linear (179.90°).

Preliminary cyclic voltammetry measurements of compounds **34** and **40** were carried out by collaborators,²⁶⁰ exhibiting irreversible oxidation events at 1.88 V and 2.71 V, respectively;

subsequent decomposition on the electrode surface prevented further investigation. Oxidation events for complexes of type $[\text{RuCl}(\text{dppe})_2(\text{C}\equiv\text{CR})]$ typically occur between -0.10 V and 1.07 V; the oxidation event observed for **40** was significantly higher, implying that the cyaphide ligand is electron-withdrawing in nature.³¹⁴ This is somewhat supported by DFT calculations, with calculations of **23b** and **41** showing a significant difference in dipole moment (1.39 and 3.55 D, respectively). Further, the calculated charge distribution of **41** implies that electron density is drawn towards the $\text{C}\equiv\text{P}$ ligand, with a net charge of -0.178 and -0.112 for the “ $\text{C}\equiv\text{P}$ ” and “ $\text{C}\equiv\text{CCO}_2\text{Et}$ ” fragments, respectively; similarly, **40** exhibits a dipole moment of 3.66 D, with net charges of -0.178 and -0.098 , respectively.

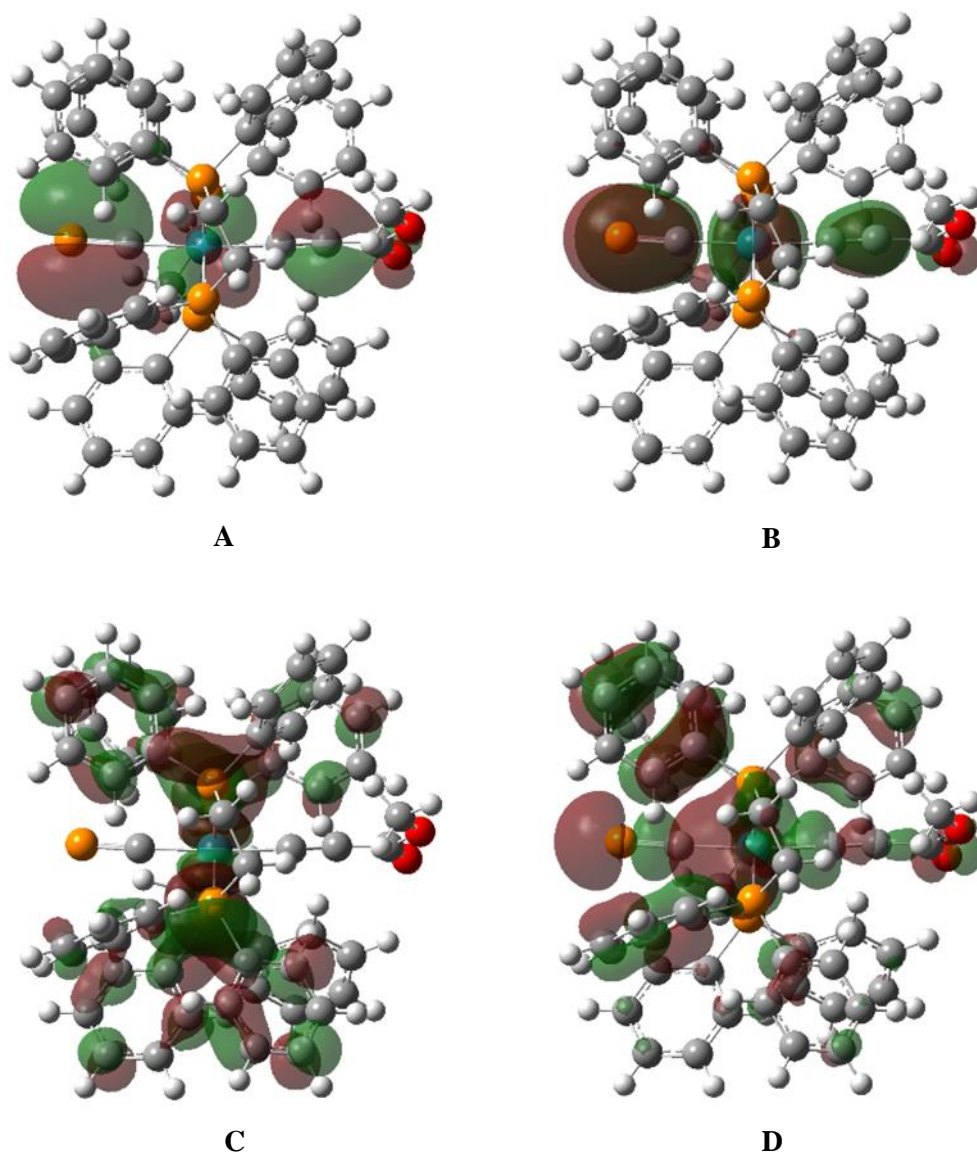


Figure 30: Plot of (A) HOMO, (B) HOMO-1, (C) LUMO, (D) HOMO-6 for **40**.

Table 17: Selected bond lengths (Å) and angles (°) for **40**, obtained by DFT calculations (B3LYP/6-31G** for H,C,P,O; LANL2DZ for Ru).

C–P	1.583
C–C	1.238
Ru–C–P	177.32
Ru–C–C	177.73

The redox properties of the anisole complexes **39** and **45** were also explored, due to the more electron-donating alkynyl ligand potentially better able to stabilise the cyaphide ligand; however, similar irreversible oxidation events were observed, with a very broad wave shape preventing assignment of the precise voltages. Interestingly, DFT studies of complex **45** demonstrate that the net charge of the C≡P moiety is -0.189 , which is not significantly different to that of complexes **40** and **41**, suggesting that the change in alkynyl ligand has had little effect on the cyaphide. This is perhaps unsurprising as NMR and IR spectroscopic data for **45** are very similar to those of **40–44**.

DFT calculations were also able to provide some insight into the structural properties of **45** in lieu of X-ray diffraction data. However, colleagues have since obtained crystals of **45**, suitable for X-ray diffraction studies, from a saturated solution of **45** in DCM and vapour diffusion of hexane (Figure 32).^{§§} These data have been included herein for comparison with DFT studies (Table 18). While the two data sets for **45** show some discrepancies, both demonstrate a greater deviation from linearity for the cyaphide and alkynyl ligands than that calculated for complex **40**. Interestingly, X-ray diffraction data for **45** demonstrate a significantly shorter C≡P bond ($1.544(4)$ Å) not only than that determined by DFT studies (1.589 Å), but also for Grützmacher's cyaphide ligand in the complex [RuH(dppe)(C≡P)] ($d_{\text{CP}} = 1.573(2)$ Å).

^{§§} Matthew C. Leech – Masters Dissertation, 2014.³²²

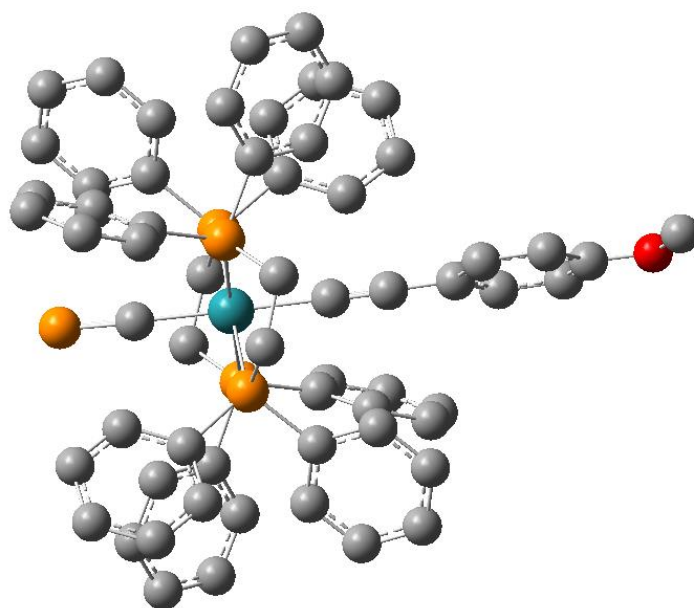


Figure 31: Optimised structure of **45** obtained through DFT calculations (B3LYP/6-31G**, LANL2DZ (Ru)).

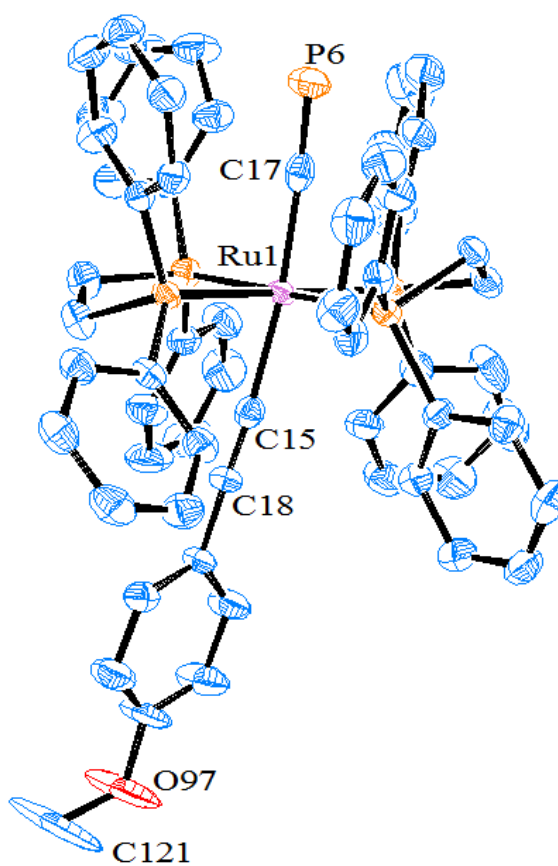


Figure 32: Molecular structure of **45**. 50% thermal ellipsoids. H atoms omitted for clarity.

Table 18: Selected bond lengths (Å) and angles (°) for **45**, obtained by both X-ray diffraction studies and DFT calculations (B3LYP/6-31G** for H,C,P,O; LANL2DZ for Ru).

	X-Ray Diffraction	DFT
C–P	1.544(4)	1.589
C–C	1.205(5)	1.234
Ru–C–P	172.3(2)	176.67
Ru–C–C	174.4(3)	177.31

4.2.3 CHEMICAL PROPERTIES AND REACTIVITY CYAPHIDE-CONTAINING COMPOUNDS

Due to the apparent electron-withdrawing nature of the cyaphide ligand, it was hypothesised that complex **40** would demonstrate an increased partial positive charge at the C=O carbon of the ester functionality compared to that of the chloride precursor (**22b**). This is somewhat supported by DFT calculations, which predict a more electropositive C=O carbon centre in **40** than **22b**, with relative Mulliken charges of approximately -0.498 and -0.443 , respectively. The apparent increase in electrophilicity of the C=O carbon centre may render the terminal cyaphide complex **40** a possible candidate for installation of a phosphalkene terminus. Both $\text{P}(\text{TMS})_3$ and $\text{LiP}(\text{TMS})_2$ were reacted with complex **40**, with a view to furnishing the complex $[\text{Ru}(\text{dppe})(\text{C}\equiv\text{P})(\text{C}\equiv\text{CC}(\text{OSiMe}_3)=\text{P}(\text{OSiMe}_3))]$. Such a complex might provide access to $[\text{Ru}(\text{dppe})(\text{C}\equiv\text{P})(\text{C}\equiv\text{CC}\equiv\text{P})]$, a desirable target in the pursuit of linear molecules with extended conjugation incorporating phosphorus. However, no reaction was observed in either case.

An alternative avenue worth pursuing in light of Angelici's work is coordination of the cyaphide to a second metal centre, either through the $\text{C}\equiv\text{P}$ π -system or the phosphorus lone pair – this reactivity was also explored. Initial investigations focused on insertion of the $\text{C}\equiv\text{P}$ bond into a metal hydride bond, a well-established synthetic route to phosphalkene formation.¹⁵⁵ However, a mixture of **40** and $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ stirred under ambient conditions for 3 h gave no reaction, which may be a result of steric bulk around the $\text{C}\equiv\text{P}$ bond, as shown in a space-filling model of the optimised structure of **40** (Figure 33). This also makes η^2 -coordination of the $\text{C}\equiv\text{P}$ bond to a second metal centre unlikely (*vide infra*), despite being the most common coordination mode for phosphalkynes. The phosphorus lone pair, however, does appear to be accessible (Figure 30); as such, continued investigation focused on η^1 -coordination.

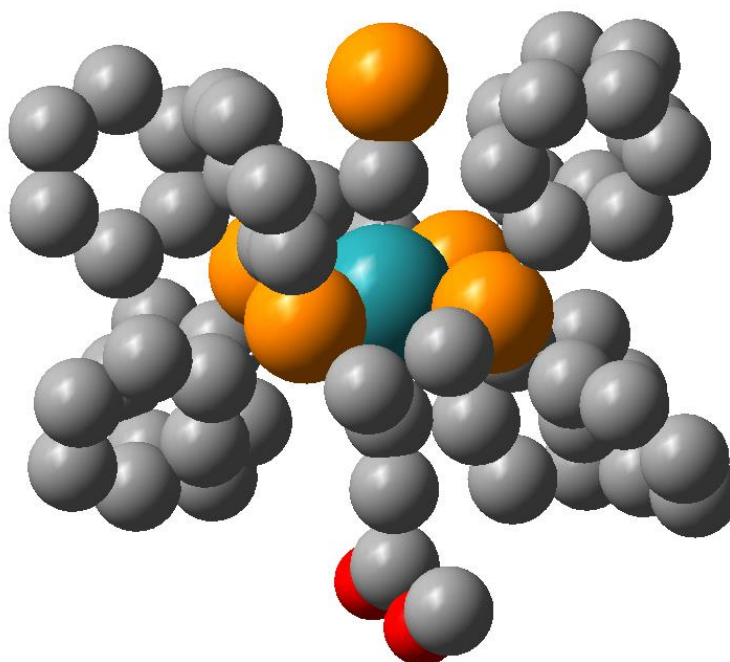


Figure 33: Optimised structure of **40** obtained by DFT calculations (B3LYP/6-31G** for H,C,P,O; LANL2DZ for Ru) depicted as a space-fill model. 100% Van der Waals radii.

Initial investigations concentrated on addition of palladium and platinum compounds to the terminal cyaphides, akin to the work of Angelici; while Angelici's cyaphide ligand was isolated only when demonstrating η^2 -coordination to a second metal centre, it is believed that the steric hindrance about the $\text{C}\equiv\text{P}$ bond in complexes **40–45** would enforce η^1 -coordination to a second metal centre.^{179,125} A mixture of **41** and $[\text{Pd}(\text{PPh}_3)_4]$ was dissolved in THF and stirred under ambient conditions for 2 h, however, no reaction was observed. A mixture of **40** and $[\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]$ stirred in THF under ambient conditions was similarly unsuccessful. Reaction of $[\text{PdCl}(\text{C}_3\text{H}_5)]_2$ with **40** exhibited multiple phosphorus environments in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the crude product after stirring for 2 h; however, no spin–spin coupling was observed between any of the phosphorus environments and an intractable mixture of products was observed in the ^1H spectrum.

With the possibility of steric hindrance still a factor, the addition of small linear molecules was considered. Au^{I} compounds have a demonstrated propensity to ligate low coordinate phosphorus compounds through the lone pair. A notable example is that of Clendenning *et al.*,²⁹ who synthesised $[\text{AuCl}(\eta^1\text{-(PC}_5\text{H}_2^t\text{Bu}_3)]$ from $[\text{AuCl}(\text{tht})]$. Therefore, **40** and $[\text{AuCl}(\text{tht})]$ were stirred in toluene under equivalent conditions, however, no reaction was observed. Another notable example of η^1 -coordination to a Au^{I} compound is the synthesis of $[\text{RuCl}_2(\text{CO})(\text{PPh}_3)_2(\text{P}(\text{Au}(\text{PPh}_3))=\text{CH}^t\text{Bu})]$ from $[\text{RuCl}(\text{CO})(\text{PPh}_3)_2(\text{P}=\text{CH}^t\text{Bu})]$ and $[\text{AuCl}(\text{PPh}_3)]$, with the success of the reaction likely due to the nucleophilicity of the lone pair

and the isolobal nature of $\text{Au}(\text{PPh}_3)^+$ and H^+ .¹⁵⁶ Given the lack of reactivity of the cyaphide ligand toward $[\text{AuCl}(\text{tbt})]$, the chloride ligand was first removed by addition of $[\text{AgBF}_4]$ to a solution of $[\text{AuCl}(\text{PPh}_3)]$ in THF. After stirring under ambient conditions for 5 min, the solution was added to **41** in THF. A colour change to yellow/green was observed upon addition, gradually changing to orange over the course of 1 h. $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy of the crude product showed a large doublet resonance at δ_{P} 40.2 ($J = 24.6$ Hz), integrating to approximately 4:1 against that of a broad singlet resonance at δ_{P} 44.9. The peak width at half-height of the latter resonance was *ca.* 25 Hz, presenting the possibility that spin–spin coupling may not have been resolved. However, a third phosphorus singlet resonance was observed at δ_{P} 47.5, which did not show any J_{PP} interactions, suggesting the presence of two phosphorus containing products. Multiple resonances, which could be attributed to dppe and OEt protons were observed in the ^1H NMR spectrum, further supporting the notion of multiple products. As such, the reaction was repeated at -78 °C and allowed to warm to ambient temperature over 1 h. A singlet resonance was observed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy at δ_{P} 44.9, similar to that seen previously; however, the other resonances demonstrated relative integrals dramatically different from those seen previously (2:1:0.3, respectively), suggesting the presence of multiple phosphorus-containing products.

Finally, the synthesis of a boron–phosphorus adduct was attempted, focusing on the boron trihalides. $\text{BF}_3 \cdot \text{Et}_2\text{O}$ was added drop-wise to a solution of **41** in THF and the mixture stirred for 1 h under ambient conditions; a gradual colour change to dark orange was observed. Two major products were evident in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, the first exhibiting broad doublet and quintet resonances at δ_{P} 45.5 and 212.6, respectively, with a mutual coupling of 10.2 Hz, consistent with a $^3J_{\text{PP}}$ coupling; these data suggest retention of the cyaphide ligand, however the relative shift of the resonance could be considered more consistent with a $\text{P}=\text{C}$ bond. The second product exhibited similar resonances, with a doublet at δ_{P} 48.8 ($J_{\text{PP}} = 10.05$ Hz) and a broad quintet at δ_{P} 239.6. $^{11}\text{B}\{^1\text{H}\}$ NMR spectroscopy shows the presence of two boron environments, with resonances at δ_{B} 19.1 and -1.1 , both consistent with 4-coordinate boron species; additionally, two broad singlet resonances were observed in the ^{19}F NMR spectrum (δ_{F} -76.6 and -76.5). The reaction was carried out at -78 °C, yielding one product preferentially, however, identical spectra were observed. Upon repeating the reaction with $[\text{Ru}(\text{dppe})_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{OMe})(\text{C}\equiv\text{P})]$ (**45**), $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy demonstrated loss of the cyaphide ligand and a new singlet resonance at δ_{P} 40.0; an intractable mixture of products was observed in the ^1H NMR spectrum. Adduct formation with a stronger Lewis acid was attempted by addition of BCl_3 to **41** in THF at -78 °C, however, multiple products were observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, with several doublets between δ_{P} 40 and 50 and a number of poorly resolved multiplets between δ_{P} 165 and 300.

4.3 CONCLUDING REMARKS

A series of ruthenium complexes bearing an η^1 -phosphaalkyne, of the type $[\text{Ru}(\text{dppe})(\text{C}\equiv\text{CR})(\text{P}\equiv\text{CSiMe}_3)]$, were prepared upon addition of $\text{P}\equiv\text{CSiMe}_3$ to complexes **22–27(b)** and exhibit comparable structural features to analogous compounds synthesised by Grützmacher and Russell.^{38,177} Subsequent addition of a base led to the synthesis of complexes bearing a cyaphide ligand, of the type $[\text{Ru}(\text{dppe})(\text{C}\equiv\text{CR})(\text{C}\equiv\text{P})]$, demonstrating only the second report of cyaphide-containing compounds to date. Again, these complexes demonstrate comparable structural properties to that previously reported. A more rapid synthesis for complexes **40–45** was observed compared to those of $[\text{RuH}(\text{dppe})(\text{C}\equiv\text{P})]$, with no intermediate species observed by NMR spectroscopy. However, a species akin to Grützmacher's intermediate was accessed upon addition of a methanolic KO^tBu solution to compound **34**, with spectroscopic data suggesting a phosphaalkenic species. DFT studies have provided further information with regard to the electronic properties of the cyaphide compounds, shedding light on the orbital distributions and molecular orbital contributions, demonstrating that the phosphorus lone pair is at a lower energy than that of the $\text{C}\equiv\text{P}$ π -bond.

Reaction of compounds **40–45** with metal complexes and boron halides showed some indication of reactivity. Attempts to incorporate a second metallic species into the cyaphide compounds were unsuccessful, potentially due to steric hinderance about the $\text{C}\equiv\text{P}$ bond. However, attempts to synthesise a Lewis adduct upon addition of $\text{BF}_3\cdot\text{Et}_2\text{O}$ demonstrated some reactivity, with a dramatic shift of the $\text{C}\equiv\text{P}$ phosphorus resonance in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum observed.

CHAPTER 5: EXPERIMENTAL

5.1 GENERAL EXPERIMENTAL DETAILS

All manipulations were carried out under a dry and oxygen-free argon or nitrogen atmosphere using standard Schlenk and inert atmosphere drybox techniques, with dried and degassed solvents, heated at reflux over the appropriate drying agents for at least 72 h before use and stored in ampoules over K mirrors or 4 Å molecular sieves under Ar. NMR spectra were obtained at 303 K, unless otherwise specified, on a VNMRs 400 MHz (^1H at 399.5 MHz, ^{31}P 161.7 MHz, ^{13}C 100.5 MHz, ^{29}Si 79.4 MHz, ^{19}F 375.9 MHz, ^{11}B 128.2 MHz and ^7Li 155.3 MHz) or 500 MHz (^1H at 499.9 MHz, ^{13}C 125.7 MHz) spectrometer and referenced by the deuterated solvent, which were purchased from GOSS Scientific. Chemical shifts are reported relative to external SiMe_4 (H, C, Si), 85% H_3PO_4 (P), CFCl_3 (F), $\text{BF}_3\cdot\text{OEt}_2$, $\text{LiCl}/\text{D}_2\text{O}$ (Li). Infrared spectra were recorded on a PerkinElmer Fourier Transform spectrometer in either solid state or in an IR solution cell with NaCl window. Mass spectra were recorded on a VG Autospec Fisons instrument or Bruker APEX III Fourier transformer mass spectrometer and carried out by Dr Ali Abdul-Sada of the departmental service. X-ray diffraction analysis was carried out on an Enraf-Nonius CAD4 system with κ CCD by Dr Mark Roe of the departmental service. Elemental analysis was carried out by Dr Stephen Boyer, London Metropolitan University Analytical Service. Raman spectra were carried out on a Nicolet Nexus FTIR/Raman by Dr A. K. Brisdon, University of Manchester. DFT calculations were performed using Gaussian 09W and visualised using GaussView 5.0, with all geometries using the B3LYP hybrid functional, with the LANL2DZ ECP basis set for ruthenium and 6-31G** for all other atoms. Optimized geometries were characterized as minima by frequency calculations with zero imaginary frequencies. Orbital distributions were calculated using GaussSum 2.2.

The following chemicals were purchased from Sigma-Aldrich, Fischer Scientific or Strem Chemicals: DABCO, $\text{Mo}(\text{CO})_6$, and $\text{W}(\text{CO})_6$ were purified by sublimation before use; $\text{IC}_6\text{H}_4\text{CO}_2\text{Me}$, $\text{IC}_6\text{H}_4\text{CO}_2\text{Et}$, TFAA, tmeda, $^n\text{BuLi}$, $\text{RuCl}_3\cdot 3\text{H}_2\text{O}$, PPh_3 , dppe, $\text{HC}\equiv\text{CCO}_2\text{Me}$, $\text{HC}\equiv\text{CCO}_2\text{Et}$, $\text{HC}\equiv\text{CSiMe}_3$, $\text{HC}\equiv\text{CPh}$, $\text{HC}\equiv\text{CC}_6\text{H}_4\text{OMe}$, HPz, HPz*, $\text{HPz}^{(\text{CF}_3)}$, $\text{HPz}^{(\text{Me},\text{CF}_3)}$, $\text{HPz}^{(\text{CF}_3)_2}$, $\text{HPz}^{(\text{tBu})}$, $\text{HPz}^{(\text{tBu})_2}$, Hmt, AgOTf, KO^tBu , CuI, $\text{Pd}(\text{PPh}_3)_4$, $\text{PdCl}_2(\text{PPh}_3)_2$, KBH_4 , $\text{HPz}^{(\text{tBu})_2}$, $\text{HPz}^{(\text{tBu})}$, TMSCH_2Cl , PCl_3 , $\text{P}(\text{SiMe}_3)_3$, BCl_3 , $\text{BF}_3\cdot\text{Et}_2\text{O}$ and $\text{AuCl}(\text{PPh}_3)$ were used as supplied. The following compounds were synthesised following literature procedures: $[\text{Ru}(\text{CO})_2(\text{PPh}_3)_3]$,³¹⁵ $[\text{RuCl}_2(\text{dppe})_2]$,²⁶⁰ $[\text{RuCl}(\text{dppe})_2][\text{OTf}]$,²⁶⁰ $\text{HC}\equiv\text{CC}_6\text{H}_4\text{CO}_2\text{Me}$,³¹⁶ $\text{HC}\equiv\text{CC}_6\text{H}_4\text{CO}_2\text{Et}$,³¹⁶ $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$,³¹⁷ $\text{PhMe}_2\text{SiCH}_2\text{Cl}$,³¹⁸ $\text{PhMe}_2\text{SiCH}_2\text{PCl}_2$,²⁰⁰ $\text{TMSCH}_2\text{PCl}_2$,²⁰⁰ KTP ,³¹⁹ KTP^* ,³²⁰ $[\text{TpW}(\text{CO})_2(\equiv\text{CC}\equiv\text{CAu}(\text{PPh}_3))]$.²⁷¹ The compounds $\text{HP}(\text{TMS})_2$, $\text{P}(\text{TMS})_3$ and $\text{AuCl}(\text{tht})$, $[\text{PdCl}(\text{C}_3\text{H}_5)]_2$, $[\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]$ were available in the lab.

5.2 EXPERIMENTAL DETAILS FOR CHAPTER 2

5.2.1 SYNTHESIS OF COMPOUNDS 2–16

Synthesis of $P\equiv CSiMe_3$

$P\equiv CSiMe_3$ was prepared by a modified literature procedure.³⁸ Typically, to a stirring solution of AgOTf (1.90 g, 7.38 mmol) in toluene (30 cm³) was added a solution of $Me_3SiCH_2PCl_2$ (0.697 g, 3.69 mmol) in toluene (5 cm³) at ambient temperature, with formation of a white precipitate observed upon mixing. The mixture was stirred for 5 min before addition of DABCO (0.83 g, 7.38 mmol) in toluene (5 cm³). The mixture was stirred for 1 h, with a colour change to beige was observed over time, before being filtered *via* cannula, furnishing an orange/red solution. To an NMR tube with Youngs' valve charged with PPh_3 (0.02 g) and C_6D_6 was added a sample of the solution (0.50 cm³), with the $^{31}P\{^1H\}$ NMR spectrum recorded at $d1 = 50$ s. The concentration of the solution was deduced by integration of the $P\equiv CSiMe_3$ and PPh_3 phosphorus resonances. $^{31}P\{^1H\}$ (C_6D_6) δ_P : 98.8 (s).

Synthesis of $P\equiv CSiMe_2Ph$

Prepared in a similar fashion to that described for $P\equiv CSiMe_3$ from AgOTf (0.702 g, 2.73 mmol), $PhMe_2SiCH_2PCl_2$ (0.343 g, 1.37 mmol) and DABCO (0.306 g, 2.73 mmol). $^{31}P\{^1H\}$ (C_6D_6) δ_P : 104.1 (s).

Synthesis of $[RuCl(CO)(PPh_3)_2(P=CH(SiMe_3))]$ (2)

To a stirring solution of $[RuHCl(CO)(PPh_3)_3]$ (1.36 g, 1.42 mmol) in DCM (5 cm³) was added a solution of $TMSC\equiv P$ (28.0 cm³, 0.051 M in toluene) at ambient temperature. The mixture was stirred for 1 h. The suspension was then filtered and solvent removed under reduced pressure. The yellow solid was triturated with hexane (30 cm³) for 1 h. The mixture was filtered and the solid dried under reduced pressure. ν_{max}/cm^{-1} 1920 (CO). 1H NMR ($CDCl_3$) δ_H : 7.98–7.10 (30 H, m, $P(C_6H_5)$), 7.28 (1 H, br, $P=CH$), -0.04 (9 H, s, $Si(CH_3)_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ_P : 544.4 (t ($J_{PP} = 8.2$ Hz)), 34.1 (d ($J_{PP} = 8.2$ Hz)).

Synthesis of [RuCl(CO)(PPh₃)₂(P=CH(SiMe₂Ph))] (3)

To a stirring solution of [RuHCl(CO)(PPh₃)₃] (0.614 g, 0.645 mmol) in DCM (30 cm³) was added a solution of PhMe₂SiC≡P (16.6 cm³, 0.039 M in toluene) at ambient temperature. The mixture was stirred for 1 h. The suspension was then filtered and solvent removed under reduced pressure. The yellow solid was triturated with hexane (30 cm³) for 1 h. The mixture was filtered and the solid dried under reduced pressure. ¹H NMR (CDCl₃) δ_H: 7.98–7.10 (30 H, m, P(C₆H₅)), 7.28 (1 H, br, P=CH), −0.04 (9 H, s, Si(CH₃)₃). ³¹P{¹H} NMR (CDCl₃) δ_P: 553.9 (t (J_{PP} = 7.7 Hz)), 33.8 (d (J_{PP} = 7.7 Hz)).

Synthesis of [Ru(CO){κ³-N,P,C-P(Pz)CH(SiMe₃)}(PPh₃)₂] (4)*

ⁿBuLi (0.05 cm³, 2.50 M in hexanes) was added drop-wise to a solution of HPz* (0.013 g, 0.130 mmol) in THF (5 cm³) and the solution stirred for 5 min before addition to a solution of **2** (0.105 g, 0.130 mmol) in THF (5 cm³) at ambient temperature. The mixture was stirred for 1 h. Solvent was removed under reduced pressure and the solid product dissolved in DCM (5 cm³). The mixture was filtered and solvent removed under reduced pressure. Yield: 0.068 g, 0.078 mmol, 60%. ν_{max}/cm^{−1} 1906 (CO). Anal Found: C, 63.35%; H, 5.44%; N, 3.32%. Calcd for (C₄₆H₄₇P₃ON₂SiRu): C, 63.52%; H, 5.41%; N, 3.22%. ¹H NMR (CD₂Cl₂) δ_H: 7.58–7.14 (30 H, m, P(C₆H₅)), 5.12 (1 H, s, Pz*-H⁴), 1.98 (3 H, br, Pz*-CH₃-5), 1.62 (1 H, m (¹J_{CH} = 123 Hz), CHSi), 0.44 (3 H, s, Pz*-CH₃-3), −0.13 (9 H, s, Si(CH₃)₃). ¹³C{¹H} NMR (CD₂Cl₂) δ_C: 210.4 (m, C≡O), 152.9 (s, Pz*-C³), 145.7 (d (J_{CP} = 1.4 Hz), Pz*-C⁵), 139.1–128.0 (m, P(C₆H₅)), 105.5 (d (J_{CP} = 2.7 Hz), Pz*-C⁴), 44.9 (ddd (J_{CP} = 78.0, 32.0, 5.1 Hz), CHSi), 12.2 (s, Pz*-CH₃-3), 9.6 (d (J_{CP} = 5.6 Hz), Pz*-CH₃-5), 2.2 (dd (J_{CP} = 5.9, 1.4 Hz), Si(CH₃)₃). ³¹P{¹H} NMR (CD₂Cl₂) δ_P: 46.6 (d (J_{PP} = 17.1 Hz)), 39.2 (dd (J_{PP} = 49.7, 17.1 Hz)), 32.9 (d (J_{PP} = 49.8 Hz), P=C). ²⁹Si{¹H} NMR (CD₂Cl₂) δ_{Si}: 1.3.

Synthesis of [Ru(CO){κ³-N,P,C-P(Pz)CH(SiMe₃)}(PPh₃)₂] (5)

Prepared in a similar fashion to **4** from HPz (0.022 g, 0.329 mmol), ⁿBuLi (0.13 cm³, 2.5 M) and **2** (0.265 g, 0.329 mmol). Yield: 0.133 g, 0.159 mmol, 48%. Anal. Found: C, 62.95%; H, 5.15%; N, 3.30%. Calcd for (C₄₄H₄₃P₃N₂OSiRu): C, 63.08%; H, 5.13%; N, 3.34%. ν_{max}/cm^{−1} 1907 (CO). ¹H NMR (CD₂Cl₂) δ_H: 7.34–6.89 (30 H, m, P(C₆H₅)), 6.89 (1 H, br, Pz-H⁴), 5.48 (1 H, br, Pz-H⁵), 5.45 (1 H, br, Pz-H³), 1.59 (1 H, br, P-CH), 0.18 (9 H, s, Si(CH₃)₃). ¹³C{¹H} NMR (CD₂Cl₂) δ_C: 211.2 (m, C≡O), 141.3 (br, Pz-C³), 135.7 (br, Pz-C⁴), 138.7–128.2 (m, P(C₆H₅)), 105.0 (br, Pz-C⁵), 47.6 (ddd (J_{CP} = 78.7, 31.3, 4.1 Hz), CHSi), 1.6 (s, Si(CH₃)₃). ³¹P{¹H} NMR (CD₂Cl₂) δ_P: 58.7 (d (J_{PP} = 46.8 Hz), P=C), 46.6 (d (J_{PP} = 17.8 Hz)), 42.0 (dd (J_{PP} = 46.8, 17.8 Hz)). ²⁹Si{¹H} NMR (CD₂Cl₂) δ_{Si}: −1.4. Crystal data for **5**: yellow rhombus, 0.2 x 0.2 x 0.1 mm³, C₄₅H₄₅Cl₂N₂OP₃RuSi, *a* = 10.8579(3) Å, *b* = 19.3948(6) Å, *c* = 20.9791(6) Å, *α* =

$84.0300(10)^\circ$, $\beta = 84.8730(10)^\circ$, $\gamma = 89.7580(10)^\circ$, $U = 4376.3(2) \text{ \AA}^3$, triclinic, $P-1$, $Z = 4$, total reflections = 58076, independent reflections = 17656, $R_{\text{int}} = 0.0534$, $\theta_{\text{max}} = 26.49$, $R_1 [I > 2\sigma(I)] = 0.0682$, $wR_2 = 0.1603$ and 988 parameters, CCDC 910162.²⁹¹

Synthesis of $[Ru(CO)\{\kappa^3\text{-}N,P,C\text{-}P(Pz^)CH(SiMe_2Ph)\}(PPh_3)_2]$ (**6**)*

Prepared in a similar fashion to **4** from HPz* (0.035 g, 0.367 mmol), ⁿBuLi (0.15 cm³, 2.5 M) and **3** (0.318 g, 0.367 mmol). Yield: 0.124 g, 0.134 mmol, 37%. Anal Found: C, 65.87%; H, 5.29%; N, 3.09%. Calcd for (C₅₁H₅₀P₃N₂OSiRu): C, 65.95%; H, 5.39%; N, 3.02%. $\nu_{\text{max}}/\text{cm}^{-1}$ 1919 (CO). ¹H NMR (CD₂Cl₂) δ_{H} : 7.50 (5 H, m, Si(P(C₆H₅)₃)), 7.36–7.14 (30 H, m, P(C₆H₅)), 5.12 (1 H, s, Pz*-H⁴), 1.98 (3 H, br, Pz*-CH₃-5), 1.77 (1 H, br (¹J_{CH} = 128.5 Hz), CHSi), 0.43 (3 H, br, Pz*-CH₃-3), 0.17 (3 H, s, Si(CH₃)₂), -0.02 (3 H, s, Si(CH₃)₂). ¹³C{¹H} NMR (CD₂Cl₂) δ_{C} : 210.1 (m, C≡O), 153.1 (s, Pz*-C³), 145.7 (d ($J_{\text{CP}} = 1.7$ Hz), Pz*-C⁵), 136.1–127.9 (m, P(C₆H₅)), 106.7 (d ($J_{\text{CP}} = 2.7$ Hz), Pz*-C⁴), 41.8 (ddd ($J_{\text{CP}} = 78.2, 32.4, 4.3$ Hz), CHSi), 12.1 (s, Pz*-CH₃-3), 9.7 (d ($J_{\text{CP}} = 5.4$ Hz), Pz*-CH₃-5), 0.5 (d ($J_{\text{CP}} = 8.8$ Hz), Si(CH₃)₂), -0.4 (d ($J_{\text{CP}} = 7.6$ Hz), Si(CH₃)₂). ³¹P{¹H} NMR (CD₂Cl₂) δ_{P} : 47.0 (d ($J_{\text{PP}} = 16.5$ Hz), P=C), 38.9 (dd ($J_{\text{PP}} = 50.7, 16.7$ Hz)), 32.3 (d ($J_{\text{PP}} = 50.2$ Hz), P=C). ²⁹Si{¹H} NMR (CD₂Cl₂) δ_{Si} : -4.9.

*Synthesis of $[Ru(CO)\{\kappa^3\text{-}N,P,C\text{-}P(Pz)CH(SiMe_2Ph)\}(PPh_3)_2]$ (**7**)*

Prepared in a similar fashion to **4** from HPz (0.020 g, 0.299 mmol), ⁿBuLi (0.12 cm³, 2.5 M) and **3** (0.260 g, 0.299 mmol). Yield: 0.137 g, 0.152 mmol, 51%. Anal Found: C, 62.35%; H, 5.04%; N, 3.52%. Calcd for (C₄₉H₄₅P₃N₂OSiRu): C, 65.41%; H, 5.01%; N, 3.11%. $\nu_{\text{max}}/\text{cm}^{-1}$ 1919 (CO). ¹H NMR (CD₂Cl₂) δ_{H} : 7.47–7.07 (30 H, m, P(C₆H₅)), 5.46 (1 H, br, Pz-H⁴), 7.52 (1 H, d ($J_{\text{HH}} = 2.08$ Hz), Pz-CH⁵), 6.81 (1 H, d ($J_{\text{HH}} = 2.08$ Hz), Pz-CH³), 1.72 (1 H, m (¹J_{CH} = 149 Hz), CHSi), 0.13 (3 H, s, Si(CH₃)₂), -0.08 (3 H, s, Si(CH₃)₂). ¹³C{¹H} NMR (CD₂Cl₂) δ_{C} : 211.1 (br, C≡O), 141.4 (s, Pz-C³), 135.9 (s, Pz-C⁵), 135.1–127.8 (m, P(C₆H₅)), 106.1 (br, Pz-C⁴), 45.1 (ddd ($J_{\text{CP}} = 3.6, 29.4, 79.5$ Hz), CHSi), 0.3 (d ($J_{\text{CP}} = 4.3$ Hz), Si(CH₃)₂), -1.6 (d ($J_{\text{CP}} = 10.4$ Hz), Si(CH₃)₂). ³¹P{¹H} NMR (CD₂Cl₂) δ_{P} : 57.0 (d ($J_{\text{PP}} = 47.1$ Hz), P=C), 47.0 (d ($J_{\text{PP}} = 17.8$ Hz)), 41.7 (dd ($J_{\text{PP}} = 47.0, 17.6$ Hz)). ²⁹Si{¹H} NMR (CD₂Cl₂) δ_{Si} : -6.6.

Synthesis of $[Ru(CO)\{\kappa^3\text{-}N,P,C\text{-}P(Pz^)CH^tBu\}(PPh_3)_2]$ (**8**)*

Prepared in a similar fashion to **4** from HPz* (0.155 g, 0.196 mmol), ⁿBuLi (0.08 cm³, 2.5 M) and **1** (0.095 g, 0.109 mmol). Yield: 0.120 g, 0.129 mmol, 66%. $\nu_{\text{max}}/\text{cm}^{-1}$ 1927 (CO). ¹H NMR (CD₂Cl₂) δ_{H} : 7.39–7.13 (30 H, m, P(C₆H₅)), 5.14 (1 H, s, Pz*-H⁴), 2.90 (1 H, ddd ($J_{\text{HP}} = 5.7, 3.3, 2.4$ Hz, ¹J_{CH} = 137 Hz), P-CH), 1.96 (3 H, s, Pz*-CH₃-5), 0.91 (9 H, s, C(CH₃)₃), 0.43 (3 H s, Pz*-CH₃-3). ¹³C{¹H} NMR (CD₂Cl₂) δ_{C} : 211.8 (m, C≡O), 152.4 (s, Pz*-C³), 145.6 (d ($J_{\text{CP}} =$

1.63 Hz), Pz*-C⁵), 134.7–134.2 (m, P(C₆H₅)), 129.5–128.0 (m, P(C₆H₅)), 105.6 (s, Pz*-C⁴), 79.8 (ddd (J_{CP} = 66.7, 37.0, 5.4 Hz), CH^tBu), 37.7 (d (J_{CP} = 13.7 Hz), C(CH₃)₃), 34.0 (dd (J_{CP} = 9.5, 3.7 Hz), C(CH₃)₃), 12.1 (s, Pz*-CH₃-3), 9.6 (d (J_{CP} = 5.3 Hz), Pz*-CH₃-5). ³¹P{¹H} NMR (CD₂Cl₂) δ_P : 45.5 (dd (J_{PP} = 17.3, 8.6 Hz)), 41.4 (dd (J_{PP} = 50.4, 17.0 Hz)), 14.7 (dd (J_{PP} = 50.4, 8.6 Hz), P=C). MS [FAB]: m/z (%): 285 (100), 850 (21) [M⁺], 751 (34) [M – Pz*]⁺, 655 (6) [M – Pz* – PC(H)^tBu].

Synthesis of [Ru(CO){ κ^3 -N,P,C-P(Pz)CH^tBu}(PPh₃)₂] (9)

Prepared in a similar fashion to **4** from HPz (0.011 g, 0.160 mmol), ⁿBuLi (0.06 cm³, 2.5 M) and **1** (0.126 g, 0.160 mmol). Yield: 0.078 g, 0.094 mmol, 59%. Anal Found: C, 62.34%; H, 5.42%; N, 3.58%. Calcd for (C₄₅H₄₃P₃N₂ORu): C, 65.77%; H, 5.24%; N, 3.41%. $\nu_{\max}/\text{cm}^{-1}$ 1906 (CO). ¹H NMR (CD₂Cl₂) δ_H : 7.36–7.10 (30 H, m, P(C₆H₅)), 6.91 (1 H, d (J_{HH} = 2.26 Hz), Pz-H³), 5.58 (1 H, br, Pz-H⁵), 5.54 (1 H, m, Pz-H⁴), 2.84 (1 H, m, P-CH), 0.88 (9 H, s, C(CH₃)₃). ¹³C{¹H} NMR (CD₂Cl₂) δ_C : 211.7 (m, C≡O), 140.9 (s, Pz-C⁵), 135.9 (s, Pz-C⁵), 138.8–128.2 (m, P(C₆H₅)), 105.2 (s, Pz-C⁴), 81.6 (ddd (J_{CP} = 68.6, 36.4, 4.8 Hz), CH^tBu), 37.7 (d (J_{CP} = 14.8 Hz), C(CH₃)₃), 33.4 (m, C(CH₃)₃). ³¹P{¹H} NMR (CD₂Cl₂) δ_P : 44.2 (dd (J_{PP} = 17.5, 8.1 Hz)), 42.5 (dd (J_{PP} = 47.1, 17.4 Hz)), 38.8 (dd (J_{PP} = 47.0, 8.2 Hz), P=C).

Synthesis of [Ru(CO){ κ^3 -N,P,C-P(Pz^{tBu})CH(SiMe₃)}(PPh₃)₂] (10)

Prepared in a similar fashion to **4** from HPz^{tBu} (0.025 g, 0.200 mmol), ⁿBuLi (0.08 cm³, 2.5 M) and **2** (0.160 g, 0.200 mmol). $\nu_{\max}/\text{cm}^{-1}$ 1909 (CO). ¹H NMR (CDCl₃) δ_H : 7.33 (6 H, s (br), C₆H₅), 7.26–7.23 (14 H, m (br), C₆H₅), 7.20–7.14 (4 H, m, C₆H₅), 7.08–7.04 (6 H, m, C₆H₅), 5.26 (1 H, s (br), Pz^{tBu}-H³), 5.15 (1 H, s (br), Pz^{tBu}-H⁴), 1.52 (1 H, m (br), CHSi), 1.17 (9 H, s, C(CH₃)₃), -0.21 (9 H, s, Si(CH₃)₃). ¹³C{¹H} NMR (CDCl₃) δ_C : 210.6 (m, C≡O), 157.8 (d ($^2J_{CP}$ = 4.0 Hz), Pz^{tBu}-C⁵), 140.0 (s, Pz^{tBu}-C³), 138.3 (d (J = 31.7 Hz), *ipso*-C₆H₅), 137.9 (dd (J = 30.8, 1.9 Hz), *ipso*-C₆H₅), 134.0–133.7 (m, C₆H₅), 128.7 (dd (J = 58.4, 1.7 Hz), C₆H₅), 128.6 (d (J = 7.2 Hz), C₆H₅), 127.8 (dd (J = 25.8, 8.9 Hz), C₆H₅), 100.8 (d ($^3J_{CP}$ = 3.3 Hz), Pz^{H,tBu}-C⁴), 46.3 (ddd (J_{CP} = 79.2, 30.9, 4.7 Hz), CHSi), 31.6 (d (br) ($^3J_{CP}$ = 1.0 Hz), C(CH₃)₃), 29.7 (d ($^4J_{CP}$ = 6.3 Hz), C(CH₃)₃), 1.2 (dd (J_{CP} = 6.0, 1.7 Hz), Si(CH₃)₃). ³¹P{¹H} NMR (CDCl₃) δ_P : 66.4 (d (J_{PP} = 46.3 Hz), P=C), 46.4 (d (J_{PP} = 18.1 Hz)), 41.4 (dd (J_{PP} = 46.3, 18.1 Hz). ²⁹Si{¹H} NMR (CDCl₃) δ_{Si} : -1.3.

Synthesis of [Ru(CO){κ³-N,P,C-P(Pz^{Me,CF₃})CH(SiMe₃)}(PPh₃)₂] (11)

Prepared in a similar fashion to **4** from HPz^(Me,CF₃) (0.036 g, 0.240 mmol), ⁿBuLi (0.10 cm³, 2.5 M) and **2** (0.193 g, 0.240 mmol). $\nu_{\max}/\text{cm}^{-1}$ 1909 (CO). ¹H NMR (CDCl₃) δ_{H} : 7.45–7.41 (6 H, m (br), C₆H₅), 7.27–7.20 (18 H, m (br), C₆H₅), 7.16–7.12 (6 H, m (br), C₆H₅), 5.52 (1 H, s, Pz^{Me,CF₃}-H⁴), 1.76 (1 H, s (¹J_{CH} = 129.3 Hz), CHSi), 0.55 (3 H, s, CH₃), -0.13 (9 H, s, Si(CH₃)₃). ¹³C{¹H} NMR (CDCl₃) δ_{C} : 209.2 (m (br), C≡O), 152.5 (m (br), Pz^{Me,CF₃}-C³), 137.8 (dd (*J* = 31.0, 1.6 Hz) Pz^{Me,CF₃}-C⁵), 134.3–133.6 (m, C₆H₅), 129.2–128.6 (m, C₆H₅), 128.0–127.7 (m, C₆H₅), 105.6 (m (br), Pz^{Me,CF₃}-C⁴), 45.2 (ddd (*J*_{CP} = 80.1, 31.8, 4.6 Hz, ¹J_{CH} = 130 Hz), SiCH), 11.8 (s, Pz^{Me,CF₃}-CH₃-3), 1.7 (dd (*J*_{CP} = 5.8, 1.4 Hz), Si(CH₃)₃). ³¹P{¹H} NMR (CDCl₃) δ_{P} : 64.6 (dq (*J*_{PP} = 46.8 Hz, ⁴*J*_{PF} = 20.2 Hz), P=C), 46.9 (dd (*J*_{PP} = 16.9, 1.1 Hz)), 38.4 (ddq (*J*_{PP} = 46.8, 16.9 Hz, ⁶*J*_{PF} = 1.8 Hz)). ²⁹Si{¹H} NMR (CDCl₃) δ_{Si} : 2.2. ¹⁹F NMR (CDCl₃) δ_{F} : -60.0 (d (⁴*J*_{FP} = 20.1 Hz)). A resonance corresponding to the CF₃ carbon could not be resolved in the ¹³C{¹H} NMR spectrum.

Synthesis of [Ru(CO){κ³-N,P,C-P(Pz^{H,CF₃})CH(SiMe₃)}(PPh₃)₂] (12)

Prepared in a similar fashion to **4** from HPz^(CF₃) (0.029 g, 0.217 mmol), ⁿBuLi (0.09 cm³, 2.5 M) and **2** (0.029 g, 0.217 mmol). Anal Found: C, 59.60%; H, 4.52%; N, 3.15%. Calcd for (C₄₅H₄₂P₃F₃N₂OSiRu): C, 59.67%; H, 4.64%; N, 3.09%. $\nu_{\max}/\text{cm}^{-1}$ 1912 (CO). ¹H NMR (CDCl₃) δ_{H} : 7.86 (2 H, m (br), Si(C₆H₅)), 7.39–7.16 (24 H, m (br), C₆H₅), 7.07 (6 H, m (br), C₆H₅), 5.59 (1 H, s, Pz^{CF₃}-H⁴), 5.28 (1 H, s, Pz^{CF₃}-H³), 1.78 (1 H, s (br), CHSi), -0.17 (9 H, s, Si(CH₃)₃). ¹³C{¹H} (CDCl₃) δ_{C} : 133.8–127.7 (m (br), C₆H₅), 0.98 (s (br), SiCH₃). ³¹P{¹H} NMR (CDCl₃) δ_{P} : 76.6 (dq (*J*_{PP} = 43.7 Hz, ⁴*J*_{PF} = 18.4 Hz), P=C), 47.7 (d (*J*_{PP} = 18.1 Hz)), 41.5 (dd (*J*_{PP} = 43.9, 18.0 Hz)). ²⁹Si{¹H} NMR (CDCl₃) δ_{Si} : -1.1. ¹⁹F NMR (CDCl₃) δ_{F} : -60.1 (d (⁴*J*_{FP} = 18.1 Hz)). Repeated attempts to obtain a ¹³C{¹H} NMR spectrum for this compound were met with limited success, with few assignable resonances resolved.

Synthesis of [Ru(CO){κ³-N,P,C-P(Pz^{Me,CF₃})CH(SiMe₂Ph)}(PPh₃)₂] (13)

Prepared in a similar fashion to **4** from HPz^(Me,CF₃) (0.022 g, 0.150 mmol), ⁿBuLi (0.06 cm³, 2.5 M) and **3** (0.130 g, 0.150 mmol). $\nu_{\max}/\text{cm}^{-1}$ 1915 (CO). ¹H NMR (CDCl₃) δ_{H} : 7.55 (2 H, m (br), Si(C₆H₅)), 7.42 (12 H, m (br), C₆H₅), 7.23 (14 H, m (br), C₆H₅), 7.15 (8 H, m (br), C₆H₅), 5.53 (1 H, s, Pz^{Me,CF₃}-H⁴), 1.97 (1 H, s (br) (¹J_{CH} = 134.52 Hz), CHSi), 0.56 (3 H, s, CH₃), 0.19 (3 H, s, Si(CH₃)), 0.00 (3 H, s, Si(CH₃)). ¹³C{¹H} NMR (CDCl₃) δ_{C} : 209.0 (m (br), C≡O), 152.6 (m (br), Pz^{Me,CF₃}-C³), 143.2 (m (br), *ipso*-C₆H₅), 134.3–133.6 (m, C₆H₅), 129.2–128.6 (m, C₆H₅), 128.0–127.5 (m, C₆H₅), 137.6 (dd (*J* = 31.1, 1.4 Hz), Pz^{Me,CF₃}-C⁵), 105.7 (m (br) (¹J_{CH} = 129 Hz), Pz^{Me,CF₃}-C⁴), 41.8 (ddd (*J*_{CP} = 80.6, 31.4, 4.9 Hz), SiCH), 11.9 (s, Pz^{Me,CF₃}-CH₃-3), 0.16 (d (³*J*_{CP} = 8.5 Hz), SiCH₃), -1.2 (d (³*J*_{CP} = 7.7 Hz), SiCH₃). ³¹P{¹H} NMR (CDCl₃) δ_{P} : 62.7 (dq

($J_{PP} = 47.1$ Hz, $^4J_{PF} = 19.7$ Hz), $P=CH$), 47.2 (d ($^2J_{PP} = 16.2$ Hz)), 38.3 (dd ($J_{PP} = 47.0, 16.5$ Hz)). $^{29}\text{Si}\{^1\text{H}\}$ NMR (CDCl_3) δ_{Si} : -6.0. ^{19}F NMR (CDCl_3) δ_{F} : -59.8 (d ($^4J_{FP} = 19.5$ Hz)). A resonance corresponding to the CF_3 carbon could not be resolved in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum.

*Synthesis of $[\text{Ru}(\text{CO})\{\kappa^3\text{-N,P,C-P}(\text{Pz}^{\text{CF}_3})\text{CH}(\text{SiMe}_2\text{Ph})\}(\text{PPh}_3)_2]$ (**14**)*

Prepared in a similar fashion to **4** from HPz^{CF_3} (0.028 g, 0.203 mmol), $^n\text{BuLi}$ (0.08 cm^3 , 2.5 M) and **3** (0.176 g, 0.203 mmol). $\nu_{\text{max}}/\text{cm}^{-1}$ 1909 (CO). ^1H NMR (CDCl_3) δ_{H} : 7.61 (2 H, m (br), $\text{Si}(\text{C}_6\text{H}_5)$), 7.41–7.18 (27 H, m (br), C_6H_5), 7.08 (6 H, m (br), C_6H_5), 5.61 (1 H, s, $\text{Pz}^{\text{H,CF}_3}\text{-H}^4$), 5.36 (1 H, s, $\text{Pz}^{\text{H,CF}_3}\text{-H}^3$), 1.97 (1 H, m (br), CHSi), 0.18 (3 H, s, $\text{Si}(\text{CH}_3)$), -0.03 (3 H, s, $\text{Si}(\text{CH}_3)$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ_{C} : 198.1 (m (br), $\text{C}\equiv\text{O}$), 142.3 (m (br), $\text{Pz}^{\text{CF}_3}\text{-C}^3$), 135.0–133.6 (m, C_6H_5), 129.9–127.3 (m, C_6H_5), 103.3 (m (br), $\text{Pz}^{\text{CF}_3}\text{-C}^4$), 46.7 (m (br), SiCH), 0.15 (d ($^3J_{CP} = 5.2$ Hz), SiCH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ_{P} : 74.9 (dq ($^2J_{PP} = 44.4$ Hz, $^4J_{PF} = 17.6$ Hz), $P=CH$), 48.0 (d ($^2J_{PP} = 17.7$ Hz)), 38.3 (dd ($^2J_{PP} = 44.4, 17.7$ Hz)). $^{29}\text{Si}\{^1\text{H}\}$ NMR (CDCl_3 , 79.4 MHz, 303 K) δ_{Si} : -5.3. ^{19}F NMR (CDCl_3) δ_{F} : -60.1 (d ($^4J_{FP} = 19.5$ Hz)). Resonances corresponding to the CF_3 and Pz-C^5 carbon atoms could not be resolved in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum.

*Synthesis of $[\text{Ru}(\text{CO})\{\kappa^3\text{-N,P,C-P}(\text{mt})\text{CH}(\text{SiMe}_3)\}(\text{PPh}_3)_2]$ (**Ru-N-15**) and*

*$[\text{Ru}(\text{CO})\{\kappa^3\text{-S,P,C-P}(\text{mt})\text{CH}(\text{SiMe}_3)\}(\text{PPh}_3)_2]$ (**Ru-S-15**)*

Prepared in a similar fashion to **4** from Hmt (0.025 g, 0.218 mmol), $^n\text{BuLi}$ (0.10 cm^3 , 2.5 M) and **2** (0.176 g, 0.218 mmol). Anal Found: C, 60.94%; H, 5.28%; N, 3.11%. Calcd for ($\text{C}_{45}\text{H}_{45}\text{P}_3\text{N}_2\text{OSiSRu}$): C, 61.15%; H, 5.17%; N, 3.21%. $\nu_{\text{max}}/\text{cm}^{-1}$ 1911 (CO). NMR spectroscopic data indicated the formation of two isomers in admixture. For both (**Ru-N-16**) and (**Ru-S-16**): ^1H NMR (CD_2Cl_2) δ_{H} : 7.55–7.14 (60 H, m, C_6H_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ_{C} : 135.8–134.2 (m, C_6H_5), 129.8–127.5 (m, C_6H_5). For (**Ru-N-16**): ^1H NMR (CD_2Cl_2) δ_{H} : 6.09 (1 H, d ($^3J_{\text{HH}} = 1.75$ Hz), mt-H^4), 5.73 (1 H, s (br), mt-H^5), 3.26 (3 H, s, mt-CH_3), 0.90 (1 H, d ($^2J_{\text{HP}} = 6.02$ Hz, $^1J_{\text{CH}} = 120.46$ Hz), CHSi), -0.17 (9 H, s, $\text{Si}(\text{CH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ_{C} : 208.2 (m, $\text{C}\equiv\text{O}$), 154.4 (m (br), mt-C^2), 130.9 (m (br), mt-C^5), 120.8 (br, mt-C^4), 36.6 (s, mt-CH_3), 28.0 (m (br)), CHSi), 2.6 (d ($^3J_{CP} = 4.58$ Hz), $\text{Si}(\text{CH}_3)_3$). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ_{P} : 44.6 (d ($^2J_{PP} = 9.6, 5.4$ Hz)), 41.7 (dd ($^2J_{PP} = 54.0, 5.4$ Hz)), 38.5 (dd ($^2J_{PP} = 54.0, 9.6$ Hz)). $^{29}\text{Si}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ_{Si} : 4.3. For (**Ru-S-15**): ^1H NMR (CD_2Cl_2) δ_{H} : 6.62 (1 H, m, mt-H^5), 6.36 (1 H, d ($^3J_{\text{HH}} = 2.16$ Hz), mt-H^4), 2.93 (3 H, s, mt-CH_3), 1.09 (1 H, m, CHSi), -0.17 (9 H, s, $\text{Si}(\text{CH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ_{C} : 163.4 (br, mt-C^2), 121.7 (d ($^2J_{CP} = 16.8$ Hz), mt-C^4), 121.4 (s, mt-C^5), 34.5 (s, mt-CH_3), 25.1 (m (br), CHSi), 2.3 (d ($^3J_{CP} = 6.1$ Hz), $\text{Si}(\text{CH}_3)_3$). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ_{P} : 85.3 (d ($^2J_{PP} = 50.0$ Hz)), 44.6 (m), 39.0 (dd ($^2J_{PP} = 50.0, 12.5$ Hz)).

$^{29}\text{Si}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ_{Si} : 3.46.

*Synthesis of $[\text{Ru}(\text{CO})\{\kappa^3\text{-N,P,C-P(mt)CH(SiMe}_2\text{Ph)}\}(\text{PPh}_3)_2]$ (**Ru-N-16**) and*

*$[\text{Ru}(\text{CO})\{\kappa^3\text{-S,P,C-P(mt)CH(SiMe}_2\text{Ph)}\}(\text{PPh}_3)_2]$ (**Ru-S-16**)*

Prepared in a similar fashion to **4** from Hmt (0.023 g, 0.198 mmol), $^n\text{BuLi}$ (0.08 cm^3 , 2.5 M) and **3** (0.172 g, 0.198 mmol). Yield: 0.077 g, 0.081 mmol, 41%. $\nu_{\text{max}}/\text{cm}^{-1}$ 1914 cm^{-1} (CO). NMR spectroscopic data indicated the formation of two isomers in admixture. For both (**Ru-N-16**) and (**Ru-S-16**): ^1H NMR (CD_2Cl_2) δ_{H} : 7.79–6.99 (70 H, m, C_6H_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ_{C} : 152.8 (m (br), mt-C), 134.7–133.8 (m, C_6H_5), 129.4–127.1 (m, C_6H_5), 121.1, 120.9 (2 x s, mt-C) 29.9, 25.8 (2 x s, CHSi), 1.2, 1.0 (2 x s (br), $\text{Si}(\text{CH}_3)_3$). For (**Ru-N-16**): ^1H NMR (CD_2Cl_2) δ_{H} : 6.03 (1 H, s, mt- H^4), 5.75 (1 H, s (br), mt- H^5), 3.20 (3 H, s, mt- CH_3), 0.99 (1 H, d ($^2J_{\text{HP}} = 6.04$ Hz), CHSi), 0.20 (3 H, s, $\text{Si}(\text{CH}_3)_3$), -0.33 (3 H, s, $\text{Si}(\text{CH}_3)_3$). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ_{P} : 44.4 (d ($^2J_{\text{PP}} = 9.4$, 5.2 Hz)), 44.0 (dd ($^2J_{\text{PP}} = 54.6$, 5.2 Hz)), 38.2 (dd ($^2J_{\text{PP}} = 54.6$, 9.4 Hz)). $^{29}\text{Si}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ_{Si} : -0.40. For (**Ru-S-16**): ^1H NMR (CD_2Cl_2) δ_{H} : 6.57 (1 H, m, mt- H^5), 6.21 (1 H, d ($^3J_{\text{HH}} = 2.16$ Hz), mt- H^4), 2.86 (3 H, s, mt- CH_3), 1.17 (1 H, m, CHSi), 0.22 (3 H, s, $\text{Si}(\text{CH}_3)_3$), -0.25 (3 H, s, $\text{Si}(\text{CH}_3)_3$). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ_{P} : 85.9 (d ($^2J_{\text{PP}} = 51.6$ Hz)), 44.6 (dd ($^2J_{\text{PP}} = 12.0$, 4.2 Hz)), 38.8 (dd ($^2J_{\text{PP}} = 51.6$, 12.0 Hz)). $^{29}\text{Si}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ_{Si} : -1.1. Full assignment of the $^{13}\text{C}\{^1\text{H}\}$ spectrum was not possible with the data obtained.

5.2.2 ADDITION OF *N*- AND *C*-DONOR NUCLEOPHILES TO COMPOUNDS **2** AND **3**, SYNTHESISING COMPOUNDS OF TYPE **A**

Synthesis of A-1

To a suspension of **2** (0.217 g, 0.027 mmol) in THF (10 cm^3) was added $\text{LiN}(\text{SiMe}_3)_2$ (0.045 g, 0.027 mmol) at ambient temperature. The mixture was stirred for 1 h and solvent removed under reduced pressure. ^1H NMR (CDCl_3) δ_{H} : 7.72 (m (br)). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ_{C} : 154.6 ($J_{\text{CP}} = 34.0$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ_{P} : 290.7 (t ($J_{\text{PP}} = 34.4$ Hz)), 18.5 (d ($J_{\text{PP}} = 34.4$ Hz)). $^{29}\text{Si}\{^1\text{H}\}$ NMR (CDCl_3) δ_{Si} : 0.02.

Synthesis of A-2

$^n\text{BuLi}$ (0.13 cm^3 , 2.5 M in hexanes) was added drop-wise to a solution of HN^iPr_2 (0.044 cm^3 , 0.032 mmol) in THF (5 cm^3) at -80 °C and the mixture allowed to stir for 20 min. The resultant solution was added to a stirring suspension of **2** (0.256 g, 0.032 mmol) in THF (10 cm^3) at ambient temperature, with a colour change from yellow to brown observed upon addition. The

mixture was allowed to warm to room temperature for 1 h. Solvent was removed under reduced pressure. ^1H NMR (CDCl_3) δ_{H} : 7.71 (d ($J = 15.7$ Hz)). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ_{C} : 154.6 (m (br)). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ_{P} : 290.7 (t ($J_{\text{PP}} = 34.7$ Hz)), 18.5 (d ($J_{\text{PP}} = 34.7$ Hz)). $^{29}\text{Si}\{^1\text{H}\}$ NMR (CDCl_3) δ_{Si} : 0.02.

Synthesis of A-3

Prepared in a similar fashion to that of **A-2** from $^n\text{BuLi}$ (0.11 cm^3 , 2.5 M in hexanes), **2** (0.213 g, 0.026 mmol) and $\text{HPZ}^{(\text{CF}_3)_2}$ (0.054 cm^3 , 0.026 mmol) at ambient temperature. ^1H NMR (CDCl_3) δ_{H} : 7.73 (d ($J = 15.71$)). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ_{C} : 154.4 ($J_{\text{CP}} = 33.4$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ_{P} : 290.7 (t ($J_{\text{PP}} = 35.0$ Hz)), 18.5 (d ($J_{\text{PP}} = 35.0$ Hz)).

Synthesis of A-4

Prepared in a similar fashion to that of **A-2** from $^n\text{BuLi}$ (0.07 cm^3 , 2.5 M in hexanes), **2** (0.152 g, 0.019 mmol) and $\text{HPZ}^{(\text{tBu})_2}$ (0.034 cm^3 , 0.019 mmol) at ambient temperature. $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectroscopy demonstrated formation of two products in admixture (**A-4** and **C-4**). For **A-4**: ^1H NMR (CDCl_3) δ_{H} : 7.72 (d ($J = 15.5$)). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ_{C} : 154.7 ($J_{\text{CP}} = 33.9$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ_{P} : 290.7 (t ($J_{\text{PP}} = 34.5$ Hz)), 18.5 (d ($J_{\text{PP}} = 34.5$ Hz)). For **C-4**: $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ_{P} : 174.5 (t ($J_{\text{PP}} = 6.8$ Hz)), 50.6 (d ($J_{\text{PP}} = 6.8$ Hz)).

Synthesis of A-5

To a solution of **2** (0.163 g, 0.202 mmol) in THF (10 cm^3) was added a solution of MeLi (0.61 cm^3 , 0.334 M in Et_2O), drop-wise, at ambient temperature. An immediate colour change to red/brown was observed. The mixture was stirred for 1 h and solvent removed under reduced pressure. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ_{P} : 290.7 (t ($J_{\text{PP}} = 34.6$ Hz)), 18.5 (d ($J_{\text{PP}} = 34.6$ Hz)).

Synthesis of A-6

Prepared in a similar fashion to **A-5** from **3** (0.124 g, 0.143 mmol) and MeLi (0.43 cm^3 , 0.334 M in Et_2O). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ_{P} : 293.7 (t ($J_{\text{PP}} = 35.0$ Hz)), 18.0 (d ($J_{\text{PP}} = 35.0$ Hz)).

Synthesis of A-7

Prepared in a similar fashion to **A-5** from **2** (0.258 g, 0.320 mmol) and MeMgBr (0.11 cm^3 , 3.0 M in Et_2O), with an immediate colour change to dark red/brown observed. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ_{P} : 287.9 (t ($J_{\text{PP}} = 33.6$ Hz)), 16.6 (d ($J_{\text{PP}} = 33.6$ Hz)).

Synthesis of A-8

Prepared in a similar fashion to **A-5** from **3** (0.090 g, 0.104 mmol) and MeMgBr (0.035 cm³, 3.0 M in Et₂O), with an immediate colour change to dark red/brown observed. ³¹P{¹H} NMR (CDCl₃) δ_P: 290.9 (t (*J*_{PP} = 34.2 Hz)), 16.2 (d (*J*_{PP} = 34.2 Hz)).

5.2.3 ADDITION OF C-DONOR NUCLEOPHILES TO COMPOUNDS **2** AND **3**, SYNTHESISING COMPOUNDS OF TYPE **B**

Synthesis of B-1

To a solution of **2** (0.090 g, 0.112 mmol) in THF (10 cm³) was added a solution of MeLi (0.33 cm³, 0.334 M in Et₂O), drop-wise, at -80 °C. The mixture was allowed to warm to ambient temperature with continual stirring for 1 h. A colour change to dark orange/red was observed. Solvent was removed under reduced pressure. ¹H NMR (CDCl₃) δ_H: 1.45 (dd (*J* = 12.56, 3.54 Hz), PCH₃), 1.08 (dd (*J* = 11.74, 3.21 Hz), RuCH₃), 0.35 (dd (*J* = 9.42, 6.37 Hz), PCH), -0.22 (s, Si(CH₃)₃). ³¹P{¹H} NMR (CDCl₃) δ_P: 33.7 (d (*J*_{PP} = 27.0 Hz), *P*_α), 30.7 (d (*J*_{PP} = 236.5 Hz) *P*_β), -4.4 (dd (*J*_{PP} = 236.5, 27.0 Hz), *P*_γ).

Synthesis of B-2

Prepared in a similar fashion to **B-1** from **2** (0.116 g, 0.144 mmol) and MeMgBr (0.048 cm³, 3.0 M in Et₂O), with a colour change to dark orange/red observed. ¹H NMR (CDCl₃) δ_H: 1.60 (dd (*J* = 12.39, 3.37 Hz), PCH₃), 1.04 (dd (*J* = 11.78, 3.20 Hz), RuCH₃), 0.35 (dd (*J* = 9.12, 6.16 Hz), PCH), -0.18 (s, Si(CH₃)₂). ³¹P{¹H} NMR (CDCl₃) δ_P: 32.1 (d (*J*_{PP} = 27.2 Hz), *P*_α), 29.6 (d (*J*_{PP} = 234.4 Hz) *P*_β), -8.1 (dd (*J*_{PP} = 234.4, 27.2 Hz), *P*_γ).

Synthesis of B-3

See synthesis of **A-6**. ¹H NMR (CDCl₃) δ_H: 1.34 (dd (*J* = 12.45, 2.63 Hz), PCH₃), 0.96 (m (br), PCH), 0.73 (dd (*J* = 12.12, 2.94 Hz), RuCH₃), 0.29, 0.16 (2 x s, Si(CH₃)₃). ³¹P{¹H} NMR (CDCl₃) δ_P: 33.6 (d (*J*_{PP} = 27.3 Hz), *P*_α), 30.9 (d (*J*_{PP} = 236.1 Hz) *P*_β), -2.9 (dd (*J*_{PP} = 236.1, 27.3 Hz), *P*_γ).

Synthesis of B-4

Prepared in a similar fashion to **B-1** from **3** (0.155 g, 0.179 mmol) and MeMgBr (0.060 cm³, 3.0

M in Et₂O), with a colour change to dark orange/red observed. ¹H NMR (CDCl₃) δ_H: 1.42 (dd (*J* = 11.89, 2.58 Hz), PCH₃), 0.90 (m (br), PCH), 0.67 (dd (*J* = 11.89, 2.57 Hz), RuCH₃), 0.10, -0.28 (2 x s, Si(CH₃)₂). ³¹P{¹H} NMR (CDCl₃) δ_P: 31.0 (d (*J*_{PP} = 27.0 Hz), *P*_α), 29.0 (d (*J*_{PP} = 234.6 Hz) *P*_β), -7.0 (dd (*J*_{PP} = 234.6, 27.0 Hz), *P*_γ).

5.2.4 ADDITION OF HPZ' TO COMPOUNDS **1**, **2** AND **3**, SYNTHESISING COMPOUNDS OF TYPES **C**, **D** AND **E**

Synthesis of C-1/D-1

HPz* (0.016 g, 0.166 mmol) and **1** (0.131 g, 0.166 mmol) were dissolved in THF (10 cm³) at ambient temperature and allowed to stir for 1 h, with a gradual colour change to yellow/orange observed. Solvent was removed under reduced pressure. For **C-1**: ¹H NMR (CDCl₃) δ_H: 2.39 (*J* = 15.07 Hz), PCH₂), 5.65 (s, Pz*-H⁴), 2.26 (s, Pz*-CH₃), 1.90 (br, PCH₂), 1.34 (s, Pz*-CH₃). ¹³C{¹H} (CDCl₃) δ_P: 149.8, 146.8 (2 x s, Pz*-C), 106.5 (s, Pz*-C⁴), 47.8 (d (*J* = 46.58 Hz), PCH₂), 30.7 (d (*J* = 8.39 Hz), C(CH₃)₃), 11.5, 10.9 (2 x s, Pz*-CH₃). ³¹P{¹H} NMR (CDCl₃) δ_P: 140.0 (d (*J*_{PP} = 7.8 Hz), PCH₂), 46.1 (d (*J*_{PP} = 7.8 Hz), PPh₃). For **D-1**: ¹H NMR (CDCl₃) δ_H: 11.51 (s, Pz*-NH), 5.26 (s, Pz*-H⁴), 1.75, 1.58 (2 x s, Pz*-CH₃). ³¹P{¹H} NMR (CDCl₃) δ_P: 44.2 (m (br), PPh₃).

Synthesis of C-2/D-2

Prepared in a similar fashion to **C-1/D-1** from HPz* (0.016 g, 0.166 mmol) and **2** (0.134 g, 0.166 mmol), furnishing a pink/orange micro-crystalline solid. For **C-2**: ³¹P{¹H} NMR (CDCl₃) δ_P: 139.7 (s, (br), PCH₂), 38.0 (s (br), PPh₃). For **D-2**: ¹H NMR (CDCl₃) δ_H: 11.47 (s, Pz*-NH), 1.72, 1.55 (2 x s, Pz*-CH₃). ³¹P{¹H} NMR (CDCl₃) δ_P: 44.2 (m (br), PPh₃). ¹H and ¹³C{¹H} NMR spectroscopy for **C-2** could not be assigned due to the small quantities of **C-2** compared to **D-2**.

Synthesis of C-3/D-3

Prepared in a similar fashion to **C-1/D-1** from HPz* (0.0073 g, 0.076 mmol) and **3** (0.066 g, 0.076 mmol), with no observable colour change. For **C-3**: ³¹P{¹H} NMR (CDCl₃) δ_P: 137.1 (s,

(br), PCH_2), 28.9 (s (br), PPh_3). For **D-3**: 1H NMR ($CDCl_3$) δ_H : 11.48 (s, Pz^*-NH), 1.73, 1.56 (2 x s, Pz^*-CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ_P : 44.2 (m (br), PPh_3). 1H and $^{13}C\{^1H\}$ NMR spectroscopy for **C-3** could not be assigned due to the small quantities of **C-3** compared to **D-3**.

Synthesis of E

$HPz^{(CF_3)_2}$ (0.026 g, 0.127 mmol) and **2** (0.102 g, 0.127 mmol) were dissolved in THF (5 cm³) at ambient temperature and allowed to stir for 1.5 h, with gradual formation of an orange/red precipitate. Solvent was removed under reduced pressure. 1H NMR ($CDCl_3$) δ_H : 6.05 (s, $Pz^{(tBu)_2}-H^4$), 2.29 (dd, $J = 13.57, 7.14$ Hz), PCH_2), 0.47 (m (br), PCH_2), -0.50 (s, $Si(CH_3)_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ_P : 254.6 (m (br), PCH_2), 31.8 (d, $J_{PP} = 32.1$ Hz), PPh_3), 31.6 (d, $J_{PP} = 18.1$ Hz), PPh_3). ^{19}F ($CDCl_3$) δ_F : 57.9 (d ($^4J_{FP} = 41.4$ Hz), $Pz-CF_3$).

5.3 EXPERIMENTAL DETAILS FOR CHAPTER 3

5.3.1 ATTEMPTED SYNTHESIS OF COMPOUNDS OF THE TYPE $[\text{RuH}(\text{CO})_2(\text{PPh}_3)_2(\text{C}\equiv\text{CR})]$ ($\text{R} = \text{CO}_2\text{H}, \text{CH}_2\text{Cl}$)

Attempted Synthesis of $[\text{RuH}(\text{CO})_2(\text{PPh}_3)_2(\text{C}\equiv\text{CCO}_2\text{H})]$

Method A: A standard solution of $\text{HC}\equiv\text{CCO}_2\text{H}$ (0.33 cm^3 , 0.34 M in DCM) was added to a suspension of $[\text{Ru}(\text{CO})_2(\text{PPh}_3)_3]$ (**17**) (0.11 g , 0.117 mmol) in DCM (15 cm^3) and the reaction allowed to stir at ambient temperature for 1 h. A colour change from yellow to brown was observed and a white solid extracted by filtration. Solvent was removed under reduced pressure.

Method B: As for Method A from $\text{HC}\equiv\text{CCO}_2\text{H}$ (0.33 cm^3 , 0.34 M in DCM) and **17** (0.10 g , 0.117 mmol) in THF (30 cm^3), furnishing $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$ (**18**). $\nu_{\text{max}}/\text{cm}^{-1}$ 1960 (RuH), 1940 (CO), 1900 (RuH). ^1H NMR (CD_2Cl_2) δ_{H} : -6.82 (1 H, m ($J_{\text{HP}} = 30, 16 \text{ Hz}$) RuH), -8.84 (1 H, m, ($J_{\text{HP}} = 74, 29 \text{ Hz}$, $J_{\text{HH}} = 6 \text{ Hz}$) RuH). Unable to determine exact aromatic resonances for PC_6H_5 due to mixture of products.

Attempted Synthesis of $[\text{Ru}(\text{TMS})(\text{CO})_2(\text{PPh}_3)_2(\text{C}\equiv\text{CCO}_2\text{H})]$

$\text{TMSC}\equiv\text{CCO}_2\text{H}$ and **17** were dissolved in THF (15 cm^3) at -70°C . The reaction mixture was allowed to warm to ambient temperature over 1 h with continual stirring. A colour change from yellow to cream was observed. The mixture was filtered and solvent removed under reduced pressure, furnishing a pale yellow oil. An intractable mixture of products was observed *via* NMR spectroscopy.

Attempted Synthesis of $[\text{RuH}(\text{CO})_2(\text{PPh}_3)_2(\text{C}\equiv\text{CCH}_2\text{Cl})]$

A standard solution of $\text{HC}\equiv\text{CCH}_2\text{Cl}$ (2.60 cm^3 , 0.28 M in THF) was added to a stirring suspension of **17** (0.10 g , 0.106 mmol) in THF (10 cm^3) at -78°C . The reaction mixture was allowed to warm to ambient temperature over 1 h. A loss of yellow colouration and formation of a white precipitate was observed over time. Formation of complexes **18** and $[\text{RuCl}(\text{CO})(\text{PPh}_3)_2(\text{CH}=\text{C}=\text{CH}_2)]$ (**19**) was confirmed by IR and NMR spectroscopy. Data for compound **19**: $\nu_{\text{max}}/\text{cm}^{-1}$ 2038 (CO), 1980 (CO). ^1H NMR (CD_2Cl_2) δ_{H} : 5.54 (1 H, m ($J = 3.5 \text{ Hz}$), RuCH), 3.26 (2 H, m ($J = 5 \text{ Hz}$), $\text{C}=\text{CH}_2$). Resonances corresponding to PC_6H_5 could not be precisely assigned due to a mixture of products in the ^1H NMR spectrum. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ_{P} : 22.3 .

5.3.2 SYNTHESIS OF COMPLEXES **22–27(a,b,c)***Synthesis of [RuCl(dppe)₂(=C=CHCO₂Me)][OTf] (**22a**)*

To a stirring solution of [RuCl(dppe)₂][OTf] (**21**) (0.760 g, 0.703 mmol) in DCM (10 cm³) was added HC≡CCO₂Me (0.126 cm³, 1.40 mmol) at ambient temperature. The solution was stirred for 16 h. Solvent was removed under reduce pressure. Yield: 0.653 g, 0.560 mmol, 80%. Anal Found: C, 58.52%; H, 4.30%. Calcd for C₅₇H₅₂P₄O₅F₃ClSRu: C, 58.69%; H, 4.46%. ¹H NMR (CDCl₃) δ_H: 7.45 (4 H, t (*J* = 6.69 Hz), C₆H₅), 7.33–7.22 (20 H, m (br), C₆H₅), 7.15 (8 H, m (br), C₆H₅), 7.07 (8 H, t (*J* = 7.55 Hz), C₆H₅), 3.42 (1 H, quint. (²*J*_{HP} = 2.36 Hz), =C=CH), 3.06 (3 H, s, OCH₃), 2.84 (8 H, m (br), C₂H₄). ¹³C{¹H} NMR (CDCl₃) δ_C: 341.6 (qnt (²*J*_{CP} = 12.8 Hz), Ru=C), 163.3 (qnt (⁴*J*_{CP} = 1.4 Hz), C=O), 133.7 (dqnt (*J* = 77.1, 2.3 Hz), C₆H₅), 131.4 (d (*J* = 68.5 Hz), C₆H₅), 130.6 (dqnt (*J* = 80.5, 11.7 Hz), ipso-C₆H₅), 128.4 (dqnt (*J* = 60.1, 2.3 Hz), C₆H₅), 105.1 (qnt (³*J*_{CP} = 1.9 Hz), Ru=C=C), 51.5 (s, CH₃), 29.0 (qnt (¹*J*_{CP} = 11.2 Hz), C₂H₄). ³¹P{¹H} NMR (CDCl₃) δ_P: 40.1.

*Synthesis of [RuCl(dppe)₂(C≡CCO₂Me)] (**22b**)*

To a stirring solution of [RuCl(dppe)₂(=C=CHCO₂Me)][OTf] (**22a**) (0.851 g, 0.703 mmol) in DCM (5 cm³) was added a solution of KO^tBu (0.157 g, 1.40 mmol) in MeOH (10 cm³). Immediate formation of a yellow precipitate was observed. The mixture was filtered immediately and the pale yellow solid washed with analytical grade MeOH (3 x 5 cm³). The solid was dried under reduced pressure. Yield: 0.434 g, 0.447 mmol, 63%. Anal. Found: C, 65.96%; H, 4.95%. Calcd for C₅₆H₅₁P₄O₂ClRu: C, 66.17%; H, 5.02%. ν_{max}/cm⁻¹ 2032 (CC). ¹H NMR (CDCl₃): δ_H 7.39–7.31 (16 H, m (br), C₆H₅), 7.23–7.19 (8 H, m (br), C₆H₅), 7.04–6.99 (16 H, m (br), C₆H₅), 3.51 (3 H, s, OCH₃), 2.69 (8 H, m, C₂H₄). ¹³C{¹H} NMR (CDCl₃): δ_C 152.8 (s, C=O), 143.1 (s (br), Ru–C≡C), 135.8 (m, ipso-C₆H₅), 135.0 (m (br), C₆H₅), 134.5 (m (br), C₆H₅), 129.5 (d (*J* = 15.1), C₆H₅), 127.8 (m (br), C₆H₅), 127.5 (m (br), C₆H₅), 107.2 (s (br), Ru–C≡C), 51.2 (s, OCH₃), 30.9 (quint. (¹*J*_{CP} = 11.8 Hz), C₂H₄). ³¹P{¹H} NMR (CDCl₃): δ_P 48.1. Crystal data for **22b**: colourless prisms, 0.2 x 0.2 x 0.08 mm³, C₅₇H₅₃Cl₃O₂P₄Ru, *a* = 22.6782(6) Å, *b* = 13.3919(3) Å, *c* = 16.9067(4) Å, α = 90°, β = 102.1390(10)°, γ = 90°, *U* = 5019.8(2) Å³, monoclinic, *Cc*, *Z* = 4, total reflections = 34498, independent reflections = 11095, *R*_{int} = 0.0708, θ_{max} = 27.47, *R*₁ [*I* > 2σ(*I*)] = 0.0530, w*R*₂ = 0.1037 and 606 parameters, CCDC 962350.²⁹¹

*Synthesis of [RuH(dppe)₂(C≡CCO₂Me)] (**22c**)*

Compound **22c** was prepared by a modified literature procedure. To a stirring solution of **21**

(0.693 g, 0.641 mmol) in DCM (20 cm³) was added HC≡CCO₂Me (0.108 cm³, 1.28 mmol) at ambient temperature. The solution was stirred for 16 h. Solvent was removed under reduced pressure and the solid triturated with hexane (20 cm³) for 30 min, with the solvent subsequently removed by cannula filtration, and the red solid dried under reduced pressure. The solid was redissolved in DCM (10 cm³) before addition of KO^tBu (0.287 g, 2.56 mmol) in MeOH (10 cm³). The solution was stirred for 16 h at ambient temperature, with gradual formation of a pale yellow precipitate. The mixture was filtered and solvent removed under reduced pressure. ¹H NMR (CDCl₃) δ_H: 7.46 (8 H, s (br), Ph), 7.34 (8 H, s (br), Ph), 7.16 (8 H, m (br), Ph), 7.09–7.00 (16 H, m (br), Ph), 3.55 (3 H, d (*J* = 7.5 Hz), CH₃), 2.56 (4 H, m (br), C₂H₄), 2.04 (4 H, m (br), C₂H₄), −9.88 (1 H, dqnt (²*J*_{HP} = 19.6 Hz, 7.5 Hz), Ru-*H*). ³¹P{¹H} NMR (CDCl₃) δ_P: 68.0.

Synthesis of [RuCl(dppe)₂(=C=CHCO₂Et)][OTf] (23a)

Prepared in a similar fashion to that described for **22a** from HCCCCO₂Et (0.210 cm³, 2.03 mmol) and **21** (1.10 g, 1.02 mmol). Yield: 1.051 g, 0.891 mmol, 87%. Anal. Found: C, 60.17%; H, 4.72%. Calcd for C₅₈H₅₄P₄O₅F₃ClSRu: C, 59.00%; H, 4.58%. ¹H NMR (CD₂Cl₂) δ_H: 7.50 (4 H, m (br), C₆H₅), 7.39 (4 H, t (*J* = 7.36 Hz), C₆H₅), 7.29 (16 H, m (br), C₆H₅), 7.20 (8 H, m (br), C₆H₅), 7.13 (8 H, t (*J* = 7.36), C₆H₅), 3.68 (2H, q (³*J*_{HH} = 6.59 Hz), OCH₂), 3.37 (1 H, qnt (⁴*J*_{HP} = 2.56 Hz), =C=CH), 2.88 (8 H, m (br), C₂H₄), 1.02 (3 H, t (³*J*_{HH} = 7.04 Hz), CH₃). ¹³C{¹H} NMR (CD₂Cl₂) δ_C: 342.1 (qnt (²*J*_{CP} = 12.7 Hz), Ru=C), 163.3 (s, C=O), 134.3 (dqnt (*J* = 78.5, 2.5 Hz), C₆H₅), 131.9 (d (*J* = 57.0), C₆H₅), 130.7 (dqnt (*J* = 84.3, 11.6 Hz), *ipso*-C₆H₅), 129.0 (dqnt (*J* = 54.9, 2.4 Hz), C₆H₅), 106.1 (s, Ru=C=C), 61.2 (s, OCH₂), 29.6 (qnt (¹*J*_{CP} = 11.3 Hz), C₂H₄), 14.60 (s, CH₃). ³¹P{¹H} NMR (CD₂Cl₂) δ_P: 40.6.

Synthesis of [RuCl(dppe)₂(C≡CCO₂Et)] (23b)

Prepared in a similar fashion to that described for **22b** from **23a** (1.20 g, 1.02 mmol) and KO^tBu (0.228 g, 2.04 mmol) in MeOH (10 cm³). Yield: 0.683 g, 0.663 mmol, 65%. Anal. Found: C, 66.35%; H, 5.01%. Calcd for C₅₇H₅₃P₄O₂ClRu: C, 66.44%; H, 5.14%. ν_{max}/cm^{−1} 2049 (CC). ¹H NMR (CDCl₃): δ_H 7.41 (8 H, m (br), C₆H₅), 7.31 (8 H, m (br), C₆H₅), 7.23 (4 H, m (br), C₆H₅), 7.18 (4 H, m (br), C₆H₅), 7.06 (8 H, m (br) C₆H₅), 6.99 (8 H, m (br) C₆H₅), 3.97 (2 H, q (¹*J*_{HH} = 7.09 Hz), OCH₂), 2.69 (8 H, m (br), C₂H₄), 1.22 (3 H, t (¹*J*_{HH} = 7.09 Hz), CH₃). ¹³C{¹H} NMR (CDCl₃): δ_C 152.2 (s, C=O), 141.3 (qnt (²*J*_{CP} = 14.7 Hz), Ru-C≡C), 135.5 (m, *ipso*-C₆H₅), 134.7 (m (br), C₆H₅), 134.2 (m (br), C₆H₅), 129.1 (d (*J* = 19.1 Hz), C₆H₅), 127.4 (m (br), C₆H₅), 127.2 (m (br), C₆H₅), 107.1 (s, Ru-C≡C), 59.3 (s, OCH₂), 30.6 (qnt (¹*J*_{CP} = 11.8 Hz), C₂H₄), 15.0 (s, CH₃). ³¹P{¹H} NMR (CDCl₃): δ_P 48.2.

Synthesis of [RuH(dppe)₂(C≡CCO₂Et)] (23c)

To a suspension of **23b** (0.075 g, 0.073 mmol) was added KO^tBu (0.033 g, 0.292 mmol) in MeOH (10 cm³) and the mixture allowed to stir at ambient temperature for 16 h. The mixture was filtered *via* cannula and the pale yellow solid product dried under reduced pressure. Anal. Found: C, 68.66%; H, 5.35%. Calcd for C₅₈H₅₄P₄O₅F₃ClSRu: C, 68.74%; H, 5.43%. ¹H-NMR (CDCl₃) δ_H: 7.45 (8 H, m (br), Ph), 7.34 (8 H, m (br), Ph), 7.16 (8 H, m (br), Ph), 7.07–7.01 (16 H, m (br), Ph), 3.98 (2 H, q, (³J_{HH} = 7.06 Hz), OCH₂), 2.57 (4 H, m (br), C₂H₄), 2.00 (4 H, m (br), C₂H₄), 1.24 (3 H, t (³J_{HH} = 7.08 Hz), CH₃), -9.92 (1 H, qnt (²J_{HP} = 19.9 Hz), Ru-H). ¹³C{¹H}-NMR (CDCl₃) δ_C: 153.3 (s, C=O), 152.1 (qnt (²J_{CP} = 12.4 Hz), Ru-C≡C), 137.8 (dqnt (*J* = 166.3, 10.7 Hz), *ipso*-C₆H₅), 133.7 (d (*J* = 13.5 Hz), C₆H₅), 128.7 (d (*J* = 12.5 Hz), C₆H₅), 127.2 (s (br), C₆H₅), 109.2 (s, Ru-C≡C), 59.9 (s, OCH₂), 33.1 (qnt (¹J_{CP} = 12.6 Hz), C₂H₄), 15.0 (s, CH₃). ³¹P{¹H} NMR (CDCl₃) δ_P: 68.0.

Synthesis of [RuCl(dppe)₂(=C=CHPh)][OTf] (24a)

Prepared in a similar fashion to that described for **22a** from HC≡CPh (0.062 cm³, 0.562 M in THF) and **21** (0.304 g, 0.281 mmol). Yield: 0.260 g, 0.220 mmol, 78%. ¹H NMR (CDCl₃) δ_H: 7.49 (1 H, d (*J*_{HH} = 7.01 Hz), Ph), 7.41–7.33 (16 H, m (br), C₆H₅), 7.28 (8 H, m (br), Ph), 7.12 (14 H, q (*J*_{HH} = 7.79 Hz), C₆H₅), 7.00 (1 H, m (br), Ph), 6.91 (1 H, t (*J*_{HH} = 7.01 Hz), Ph), 6.80 (2 H, t (*J*_{HH} = 7.79 Hz), C₆H₅), 5.78 (2 H, d (*J*_{HH} = 7.79 Hz), 3.31 (1 H, qnt (³J_{HP} = 2.34 Hz), =C=CH), 2.97–2.78 (8 H, m (br), C₂H₄). ³¹P{¹H} NMR (CDCl₃) δ_P: 39.4.

Synthesis of [RuCl(dppe)₂(C≡CPh)] (24b)

Prepared by a modified literature procedure in a similar fashion to that described for **22b** from **24a** (0.640 g, 0.541 mmol) and KO^tBu (0.030 g, 0.271 mmol) in MeOH (10 cm³). Yield: 0.243 g, 0.235 mmol, 87%. ¹H NMR (CDCl₃): δ_H 7.60 (8 H, m (br), C₆H₅), 7.56 (1 H, m (br), Ph), 7.28 (8 H, m (br), C₆H₅), 7.20 (t (*J*_{HH} = 7.40 Hz), C₆H₅), 7.14 (3 H, m (br), C₆H₅), 7.00 (14 H, q (*J*_{HH} = 7.79 Hz) C₆H₅), 6.77 (1 H, m (br), Ph), 6.71 (2 H, q (*J*_{HH} = 7.79 Hz), Ph), 2.71 (8 H, m (br), C₂H₄). ³¹P{¹H} NMR (CDCl₃): δ_P 49.6.

Synthesis of [RuH(dppe)₂(C≡CPh)] (24c)

Prepared by a modified literature procedure in a similar fashion to that described for **23c** from **24b** (0.240 g, 0.203 mmol) and KO^tBu (0.023 g, 0.203 mmol) in MeOH (10 cm³). **24c** formed in admixture with **24b**: ¹H NMR (CDCl₃) δ_H: 7.55 (10 H, m (br), C₆H₅), 7.49 (20 H, m (br), C₆H₅), 7.27–7.23 (4 H, m (br), C₆H₅), 7.19–7.13 (20 H, m (br), C₆H₅), 7.06 (12 H, t (*J*_{HH} = 7.52 Hz), C₆H₅), 7.00–6.96 (22 H, m (br), C₆H₅), 6.79 (2 H, d (*J*_{HH} = 7.25 Hz), C₆H₄), 2.65 (8 H, m

(br), C₂H₄), 2.52 (4 H, m (br), C₂H₄), 2.01 (4 H, m (br), C₂H₄), -10.28 (1 H, qnt (²J_{HP} = 20.15 Hz), Ru-H). ³¹P{¹H} NMR (CDCl₃) δ_P: 68.5 (s), 49.6 (s).

Synthesis of [RuCl(dppe)₂(=C=CHC₆H₄CO₂Me)][OTf] (25a)

Prepared by a modified literature procedure in a similar fashion to that described for **22a** from HC≡CC₆H₄OMe (0.300 g, 1.75 mmol) in THF) and **21** (0.944 g, 0.872 mmol). Yield: 0.837 g, 0.674 mmol, 73%. ¹H-NMR (CDCl₃) δ_H: 7.33–7.23 (24 H, dt (J_{HH} = 36.98, 7.40 Hz), 7.18 (2 H, d (³J_{HH} = 8.17 Hz), C₆H₄), 7.11–7.02 (16 H, m (br), C₆H₅), 7.68 (2 H, d (³J_{HH} = 8.17 Hz), C₆H₄), 4.48 (1 H, m (br), =CH), 3.81 (3 H, s, CH₃), 2.93 (8 H, m (br), C₂H₄). ³¹P{¹H} NMR (CDCl₃) δ_P: 36.1.

Synthesis of [RuCl(dppe)₂(C≡CC₆H₄CO₂Me)] (25b)

Prepared by a modified literature procedure in a similar fashion to that described for **22b** from **25a** (0.705 g, 0.581 mmol) and KO^tBu (0.033 g, 0.290 mmol) in MeOH (10 cm³). ³¹P{¹H} and ¹H NMR spectroscopy demonstrates the formation of **25b** in admixture with **25c** (ca. 1:2.5). NMR spectroscopy data for **25b**: ¹H NMR (CDCl₃): δ_H 7.76 (2 H, d (³J_{HH} = 8.36 Hz), C₆H₄), 7.49–6.92 (40 H, m (br), C₆H₅), 6.57 (2 H, d (³J_{HH} = 8.36 Hz), C₆H₄), 3.89 (3 H, s, CH₃), 2.69 (8 H, m (br), C₂H₄). ³¹P{¹H} NMR (CDCl₃): δ_P 49.0. Aryl resonances for PPh₃ groups could not be precisely assigned as **25b** was formed in admixture with **25c**.

Synthesis of [RuH(dppe)₂(C≡CC₆H₄CO₂Me)] (25c)

Prepared in a similar fashion to that described for **23c** from **25b** (0.145 g, 0.136 mmol) and KO^tBu (0.061 g, 0.545 mmol) in MeOH (10 cm³). Anal Found: C, 70.24%; H, 5.21%. Calcd for C₆₂H₅₆P₄O₂Ru: C, 70.39%; H, 5.30%. ν_{max}/cm⁻¹ 2049 (CC). ¹H-NMR (CDCl₃) δ_H: 7.89 (2 H, d (³J_{HH} = 8.30 Hz), C₆H₄), 7.47–7.41 (16 H, m (br), C₆H₅), 7.16–7.13 (8 H, m (br), C₆H₅), 7.07–7.03 (10 H, m (br), C₆H₅), 6.97–6.94 (9 H, m (br), C₆H₅), 3.92 (3 H, s, CH₃), 2.47 (4 H, m (br), C₂H₄), 2.00 (4 H, m (br), C₂H₄), -10.06 (1 H, qnt (²J_{HP} = 19.67 Hz), Ru-H). ¹³C{¹H} NMR (CDCl₃) δ_C: 167.9 (s, C=O), 147.2 (qnt (²J_{CP} = 13.1 Hz), Ru-C≡C), 138.3 (dqnt (J = 126.73, 10.01 Hz), *ipso*-C₆H₅), 136.6 (s, C-C=O), 133.8 (dqnt (J = 18.9, 2.6 Hz), C₆H₅), 129.8 (s, C₆H₄), 129.3 (s, C₆H₄), 128.6 (d (J = 18.9 Hz), C₆H₅), 127.1 (dm (J = 11.0 Hz)), 123.2 (s, Ru-C≡C), 117.8 (s, C≡C-C), 51.8 (s, CH₃), 32.9 (qnt (¹J_{CP}) = 12.9 Hz), C₂H₄). ³¹P{¹H} NMR (CDCl₂) δ_P: 68.5.

Synthesis of [RuCl(dppe)₂(=C=CHC₆H₄CO₂Et)][OTf] (26a)

Prepared in a similar fashion to that described for **22a** from HC≡CC₆H₄CO₂Et (2.89 cm³, 0.197 M in THF) and **21** (0.308 g, 0.285 mmol). Yield: 0.216 g, 0.172 mmol, 60%. Anal. Found: C, 61.01%; H, 4.69%. Calcd for C₅₈H₅₄P₄O₅F₃ClSRu: C, 61.17%; H, 4.62%. ¹H-NMR (CDCl₃) δ_H: 7.33 (10 H, m (br), C₆H₅), 7.24 (10 H, m (br), C₆H₅), 7.19 (2 H, d (³J_{HH} = 8.43 Hz), C₆H₄), 7.08 (16 H, dt (*J* = 19.11, 7.88 Hz), C₆H₅), 5.69 (2 H, d (³J_{HH} = 8.38 Hz), C₆H₄), 4.63 (1 H, qnt (³J_{HP} = 2.56 Hz), =C=CH), 4.27 (2 H, q (³J_{HH} = 7.13 Hz), OCH₂), 2.93 (8 H, m (br), C₂H₄), 1.34 (3 H, t (³J_{HH} = 7.22 Hz), CH₃). ¹³C{¹H} NMR (CDCl₃) δ_C: 355.5 (m (br), Ru=C), 166.3 (s, C=O), 133.7 (dqnt (*J* = 101.5, 2.1 Hz), C₆H₅), 131.8 (m (br), C₆H₅), 131.1 (d (*J* = 45.6), C₆H₅), 128.5 (dqnt (*J* = 85.4, 2.1 Hz), C₆H₅), 126.8 (s, C₆H₄), 109.2 (s, Ru=C=C), 60.8 (s, OCH₂), 29.2 (qnt (¹J_{CP} = 11.2 Hz), C₂H₄), 14.5 (s, CH₃). ³¹P{¹H} NMR (CDCl₃) δ_P: 36.1.

Synthesis of [RuCl(dppe)₂(C≡CC₆H₄CO₂Et)] (26b)

Prepared in a similar fashion to that described for **22b** from **26a** (0.136 g, 0.109 mmol) and KO^tBu (0.006 g, 0.054 mmol) in MeOH (10 cm³). Yield: 0.043 g, 0.039 mmol, 36 %. ν_{max}/cm⁻¹ 2045 (CC). ¹H-NMR (CDCl₃) δ_H: 7.77 (2 H, d (³J_{HH} = 8.35 Hz), C₆H₄), 7.43 (8 H, m (br), C₆H₅), 7.33 (8 H, m (br), C₆H₅), 7.19 (8 H, q (*J* = 7.77 Hz), C₆H₅), 7.01 (16 H, dt (*J* = 26.89, 7.48 Hz), C₆H₅), 6.58 (2 H, d (³J_{HH} = 8.29 Hz), C₆H₄), 4.35 (2 H, q, (³J_{HH} = 7.18 Hz), OCH₂), 2.69 (8 H, m (br), C₂H₄), 1.40 (3 H, t (³J_{HH} = 7.01 Hz), CH₃). ¹³C{¹H} NMR (CDCl₃) δ_C: 167.3 (s, C=O), 136.0 (m (br), Ru-C≡C), 136.0 (dqnt (*J* = 60.7, 10.3 Hz), *ipso*-C₆H₅), 135.1 (s, C₆H₄), 134.6 (m, C₆H₅), 134.3 (m, C₆H₅), 129.8 (s, C₆H₄), 129.0 (s, C₆H₄), 129.0 (m, C₆H₅), 127.4 (m, C₆H₅), 127.2 (m, C₆H₅), 124.1 (s, C₆H₄), 115.0 (s, Ru-C≡C), 60.6 (s, OCH₂), 30.8 (qnt (¹J_{CP} = 11.76 Hz), C₂H₄), 14.6 (s, CH₃). ³¹P{¹H} NMR (CD₂Cl₂) δ_P: 49.1.

Synthesis of [RuH(dppe)₂(C≡CC₆H₄CO₂Et)] (26c)

Prepared in a similar fashion to that described for **23c** from **26b** (0.216 g, 0.172 mmol) and KO^tBu (0.077 g, 0.688 mmol) in MeOH (10 cm³). Anal Found: C, 70.37%; H, 5.58%. Calcd for C₆₂H₅₈P₄O₂Ru: C, 70.25%; H, 5.48%. ν_{max}/cm⁻¹ 2040 (CC). ¹H NMR (CDCl₃) δ_H: 7.92 (2 H, d (³J_{HH} = 8.42 Hz), C₆H₄), 7.49–7.43 (16 H, m (br), C₆H₅), 7.16 (8 H, m (br), C₆H₅), 7.08 (10 H, q (*J* = 7.35 Hz), C₆H₅), 6.98 (8 H, t (*J* = 7.61 Hz), C₆H₅), 4.40 (2 H, q, (³J_{HH} = 7.11 Hz), OCH₂), 2.49 (4 H, m (br), C₂H₄), 2.01 (4 H, m (br), C₂H₄), 1.40 (3 H, t (³J_{HH} = 7.11 Hz), CH₃), -10.05 (1 H, qnt (²J_{HP} = 19.82 Hz), Ru-H). ¹³C{¹H} NMR (CDCl₃) δ_C: 167.4 (s, C=O), 146.7 (qnt (²J_{CP} = 13.0 Hz), Ru-C≡C), 138.3 (dqnt (*J* = 126.8, 9.7 Hz), *ipso*-C₆H₅), 136.5 (s, C-C=O), 133.9 (d (*J* = 19.0 Hz), C₆H₅), 129.8 (s, C₆H₄), 129.3 (s, C₆H₄), 128.5 (d (*J* = 19.0 Hz), C₆H₅), 127.1 (d (*J* = 10.2 Hz), C₆H₅), 123.6 (s, Ru-C≡C), 117.7 (s, C≡C-C), 60.5 (s, OCH₂), 33.1 (qnt (¹J_{CP} = 12.5 Hz), C₂H₄), 14.7 (s, CH₃). ³¹P{¹H} NMR (CDCl₂) δ_P: 68.5.

Synthesis of [RuCl(dppe)₂(=C=CHC₆H₄OMe)][OTf] (27a)

Prepared by a modified literature procedure in a similar fashion to that described for **22a** from HC≡CC₆H₄OMe (0.24 cm³, 1.86 mmol) and **21** (1.01 g, 0.931 mmol). Yield: 1.11 g, 0.917 mmol, 98 %. ¹H NMR (CDCl₃) δ_H: 7.35–7.27 (24 H, m (br), C₆H₅), 7.11–7.07 (16 H, m (br), C₆H₅), 6.28 (2 H, d (³J_{HH} = 8.33 Hz) C₆H₄), 5.70 (2 H, d (³J_{HH} = 8.33 Hz) C₆H₄), 3.73, (1 H, m (br), =CH), 3.67 (3 H, s, CH₃), 2.95 (4 H, m (br), C₂H₄), 2.81 (4 H, m (br), C₂H₄). ³¹P{¹H} NMR (CDCl₃) δ_P: 38.4.

Synthesis of [RuCl(dppe)₂(C≡CC₆H₄OMe)] (27b)

Prepared by a modified literature procedure in a similar fashion to that described for **22b** from **27a** (1.11 g, 0.917 mmol) and KO^tBu (0.051 g, 0.466 mmol) in MeOH (10 cm³). Yield: 0.312 g, 0.293 mmol, 32%. ¹H NMR (CDCl₃): δ_H 7.59 (8 H, m (br), C₆H₅), 7.28 (8 H, m (br), C₆H₅), 7.19 (8 H, m (br), C₆H₅), 7.04–6.97 (16 H, m (br), C₆H₅), 6.71 (2 H, d (³J_{HH} = 8.56 Hz) C₆H₄), 6.66 (2 H, d (³J_{HH} = 8.56 Hz) C₆H₄), 3.81 (3 H, s, CH₃), 2.70 (8 H, m (br), C₂H₄). ³¹P{¹H} NMR (CDCl₃): δ_P 49.0.

Synthesis of [RuH(dppe)₂(C≡CC₆H₄OMe)] (27c)

Prepared in a similar fashion to that described for **23c** from **27b** (0.145 g, 0.136 mmol) and KO^tBu (0.061 g, 0.545 mmol) in MeOH (10 cm³). ν_{max}/cm⁻¹ 2049 (CC). ¹H NMR (CDCl₃) δ_H: 7.47 (16 H, m (br), C₆H₅), 7.14 (8 H, t (J_{HH} = 7.29 Hz), C₆H₅), 7.10 (2 H, d (³J_{HH} = 8.65 Hz), C₆H₄), 7.09 (8 H, t (J_{HH} = 7.29 Hz), C₆H₅), 6.97 (8 H, t (J_{HH} = 7.45 Hz), C₆H₅), 6.82 (2 H, d (³J_{HH} = 8.65 Hz), C₆H₄), 3.84 (3 H, s, CH₃), 2.49 (4 H, m (br), C₂H₄), 1.98 (4 H, m (br), C₂H₄), -10.37 (1 H, qnt (²J_{HP} = 19.78 Hz), Ru-H). ¹³C{¹H} NMR (CDCl₃) δ_C: 155.6 (s, C₆H₄), 138.7 (dqnt (¹J_{CP} = 125.2, 9.5 Hz), *ipso*-C₆H₅), 134.0 (dqnt (J = 26.8, 2.8 Hz), C₆H₅), 131.0 (s, C₆H₄), 129.5 (qnt (²J_{CP} = 13.8 Hz), Ru-C≡C), 128.4 (d (J = 24.2 Hz), C₆H₅), 127.0 (dm (J = 14.3 Hz), C₆H₅), 125.1 (s, C₆H₄), 114.8 (s, Ru-C≡C), 113.5 (s, C₆H₄), 55.5 (s, CH₃), 33.12 (qnt (¹J_{CP} = 12.6 Hz), C₂H₄). ³¹P{¹H} NMR (CDCl₃) δ_P: 68.5.

Synthesis of [RuCl(dppe)₂(=C=CHCH₂Cl)][OTf] (28a)

Prepared in a similar fashion to that described for **22a** from HC≡CCH₂Cl (0.57 cm³, 0.28 M in THF) and **21** (0.174 g, 0.161 mmol). Yield: 0.149 g, 0.129 mmol, 80%. Anal. Found: C, 58.13%; H, 4.51%. Calcd for C₅₆H₅₁P₄O₃F₃Cl₂SRu: C, 58.13%; H, 4.41%. ¹H NMR (CDCl₃) δ_H: 7.45 (4 H, m (br), C₆H₅), 7.45 (4 H, m (br), C₆H₅), 7.32–7.26 (24 H, m (br), C₆H₅), 7.21 (4 H, m (br), C₆H₅), 7.07 (8 H, m (br), C₆H₅), 3.06 (2 H, d (³J_{HH} = 9.16 Hz), CH₂), 2.87 (8 H, m (br), C₂H₄), 2.64 (1 H, tqnt (³J_{HH} = 9.16 Hz; ⁴J_{PH} = 2.7 Hz), =C=CH). ¹³C{¹H} NMR (CDCl₃) δ_C:

345.8 (qnt ($^2J_{\text{CP}} = 13.2$ Hz), Ru=C), 134.0 (m, C₆H₅), 133.3 (m, C₆H₅), 131.3 (d ($J = 71.7$ Hz), C₆H₅), 129.1 (m, C₆H₅), 128.2 (m, C₆H₅), 131.3 (dqnt ($J = 60.2, 11.3$ Hz), *ipso*-C₆H₅), 104.9 (m (br), Ru=C=C), 35.3 (s, CH₂Cl), 29.2 (qnt ($^1J_{\text{CP}} = 11.4$ Hz), C₂H₄). $^{31}\text{P}\{^1\text{H}\}$ -NMR (CDCl₃) δ_{P} : 41.5.

Attempted synthesis of [RuCl(dppe)₂(C≡CCH₂Cl)] (28b)

Method A: To a stirring solution of **21** (0.308 g, 0.285 mmol) in DCM (5 cm³) was added a standard solution of HC≡CCH₂Cl (1.02 cm³, 0.28 M in THF) and the solution allowed to stir for 16 h furnishing a green/brown solution. Subsequently, a solution of KO^tBu (0.064 g, 0.285 mmol) in MeOH (10 cm³) was added and left stirring for 16 h. Immediate formation of a yellow/green precipitate was observed. The mixture was filtered and the solid washed with analytical grade MeOH (3 x 5 cm³). The solid was dried under reduced pressure. NMR spectroscopic data was consistent with formation of compounds **28b** and [RuH(dppe)₂(C≡CCH₂Cl)] (**28c**) in admixture, with a third unknown species observed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. ^1H (CD₂Cl₂) δ_{H} : 7.50–6.96 (m, C₆H₅), 3.32 (s, CH₂Cl), 3.08 (CH₂Cl), 2.70 (8 H, m (br), C₂H₄), 2.56 (4 H, m (br), C₂H₄), 2.04 (4 H, m (br), C₂H₄). $^{31}\text{P}\{^1\text{H}\}$ (CD₂Cl₂) δ_{P} : 68.1 (s, RuH(dppe)), 49.0 (s, RuCl(dppe)), 44.2 (s). ^1H NMR spectroscopic data for **28b** and **28c** could not be distinguished between.

Method B: To a stirring solution of **21** (0.337 g, 0.312 mmol) in DCM (5 cm³) was added a standard solution of HC≡CCH₂Cl (1.11 cm³, 0.28 M in THF) and the solution allowed to stir for 16 h furnishing a green/brown solution. Subsequently, a solution of KO^tBu (0.105 g, 0.623 mmol) in MeOH (10 cm³) was added and left stirring for 16 h. Immediate formation of a yellow/green precipitate was observed. The mixture was filtered and the solid washed with analytical grade MeOH (3 x 5 cm³). The solid was dried under reduced pressure. $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectroscopy demonstrated the same product mixture as that for Method A.

5.3.3 ATTEMPTED SYNTHESIS OF BIS(ALKYNYL) COMPLEXES

Attempted synthesis of [Ru(dppe)₂(C≡CO₂Me)₂]

Method A: AgOTf (0.074 g, 0.289 mmol) and [RuCl₂(dppe)₂] (**20**) (0.140 g, 0.144 mmol) were dissolved in DCM (5 cm³) and stirred for 15 min at ambient temperature, with subsequent addition of HC≡CCO₂Me (0.052 cm³, 0.578 mmol). The reaction mixture was stirred for 16 h at ambient temperature. The resultant pale green/brown mixture was filtered and solvent removed under reduced pressure. $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectroscopy demonstrated formation of

unknown species **F-1**. $^{31}\text{P}\{^1\text{H}\}$ (CDCl_3) δ_{P} : 61.5 (ddd ($J_{\text{PP}} = 234.9, 25.1, 13.9$ Hz), 60.3 (ddd ($J_{\text{PP}} = 23.4, 15.6, 13.9$ Hz)), 55.5 (ddd ($J_{\text{PP}} = 234.9, 23.4, 8.7$ Hz)), 40.9 (ddd ($J_{\text{PP}} = 25.1, 15.6, 8.7$ Hz)).

Attempted synthesis of $[\text{Ru}(\text{dppe})_2(\text{C}\equiv\text{CO}_2\text{Et})_2]$

Method A: AgOTf (0.063 g, 0.244 mmol) and **20** (0.118 g, 0.122 mmol) were dissolved in DCM (5 cm^3) and stirred for 15 min. at ambient temperature, with subsequent addition of $\text{HC}\equiv\text{CCO}_2\text{Et}$ (0.049 cm^3 , 0.487 mmol). The reaction mixture was stirred for 16 h at ambient temperature. The resultant pale green/brown mixture was filtered and solvent removed under reduced pressure. $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectroscopy demonstrated formation of unknown species **F-2**. $^{31}\text{P}\{^1\text{H}\}$ (CDCl_3) δ_{P} : 62.0 (ddd ($J_{\text{PP}} = 235.8, 25.1, 13.9$ Hz), 60.1 (ddd ($J_{\text{PP}} = 25.1, 15.6, 13.9$ Hz)), 54.2 (ddd ($J_{\text{PP}} = 235.8, 24.3, 8.7$ Hz)), 40.9 (ddd ($J_{\text{PP}} = 25.1, 15.6, 8.7$ Hz)).

Method B: $\text{HC}\equiv\text{CCO}_2\text{Et}$ (0.098 cm^3 , 0.974 mmol) and **20** (0.236 g, 0.244 mmol) were dissolved in DCM (5 cm^3) and stirred for 15 min. at ambient temperature, with subsequent addition of AgOTf (0.125 g, 0.487 mmol). The reaction mixture was stirred for 16 h at ambient temperature. The mixture was filtered and solvent removed under reduced pressure. $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectroscopy demonstrated formation of **23a**. The resultant product was redissolved in DCM (5 cm^3), with subsequent addition of a solution of KO^tBu (0.109 g, 0.974 mmol) in MeOH (10 cm^3). $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectroscopy demonstrated formation of **23b** and **23c**.

Method C: $\text{HC}\equiv\text{CCO}_2\text{Et}$ (0.045 cm^3 , 0.442 mmol) and **20** (0.107 g, 0.110 mmol) were dissolved in DCM (5 cm^3) and stirred for 15 min. in an IMS bath to maintain a constant temperature of 21 °C, with subsequent addition of AgOTf (0.057 g, 0.220 mmol). The reaction mixture was stirred for 72 h at ambient temperature. The mixture was filtered and solvent removed under reduced pressure. $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectroscopy demonstrated formation of **23a** (major product) and unknown species **F-2** (minor product).

Method D: $\text{HC}\equiv\text{CCO}_2\text{Et}$ (0.060 cm^3 , 0.599 mmol) and **20** (0.145 g, 0.149 mmol) were dissolved in DCM (5 cm^3) and stirred for 15 min at 0 °C, with subsequent addition of AgOTf (0.077 g, 0.299 mmol). The mixture was allowed to warm to ambient temperature over 16 h with continual stirring. The mixture was filtered and solvent removed under reduced pressure. NMR spectroscopic data demonstrated formation of compound **F-2** (major product) and **23a** (minor product).

Method E: $\text{HC}\equiv\text{CCO}_2\text{Et}$ (0.047 cm^3 , 0.462 mmol) and **20** (0.112 g, 0.116 mmol) were dissolved in DCM (5 cm^3) and stirred for 15 min at -30 °C, with subsequent addition of AgOTf (0.059 g, 0.231 mmol). The mixture was allowed to warm to 12 °C over 16 h with continual stirring, before filtering. Solvent was removed under reduced pressure. NMR spectroscopic data demonstrated formation of compound **F-2** (major product) and **23a** (minor product).

Attempted synthesis of $[Ru(dppe)_2(C\equiv CC_6H_4CO_2Me)_2]$

Method B: $HC\equiv CC_6H_4CO_2Me$ (0.132 g, 0.772 mmol), **20** (0.187 g, 0.193 mmol), and AgOTf (0.100 g, 0.386 mmol) were dissolved in DCM (5 cm³) and stirred for 24 h at ambient temperature. The mixture was subsequently filtered and solvent removed under reduced pressure. ³¹P{¹H} and ¹H NMR spectroscopy demonstrated formation of **25a**. The resultant product was redissolved in DCM (5 cm³), with subsequent addition of a solution of KO^tBu (0.086 g, 0.772 mmol) in MeOH (10 cm³). ³¹P{¹H} and ¹H NMR spectroscopy demonstrated formation of **25b** and **25c**.

Attempted synthesis of $[Ru(dppe)_2(C\equiv CCO_2Me)(C\equiv CC_6H_4CO_2Me)]$

Method A: $HC\equiv CC_6H_4CO_2Me$ (0.093 g, 0.545 mmol), **20** (0.264 g, 0.272 mmol), and AgOTf (0.140 g, 0.545 mmol) were dissolved in DCM (10 cm³) with immediate addition of $HC\equiv CCO_2Me$ (0.049 cm³, 0.545 mmol) and stirred for 16 h at ambient temperature. The resultant dark red mixture was subsequently filtered and solvent removed under reduced pressure. ³¹P{¹H} and ¹H NMR spectroscopy demonstrated formation of **22a**. The resultant product was redissolved in DCM (5 cm³), with subsequent addition of a solution of KO^tBu (0.122 g, 1.09 mmol) in MeOH (10 cm³). ³¹P{¹H} and ¹H NMR spectroscopy demonstrated formation of **22b** and **22c**.

Method B: AgOTf (0.008 g, 0.029 mmol) and **22b** (0.030 g, 0.029 mmol) were dissolved in DCM (5 cm³) and the mixture stirred for 5 min at ambient temperature. Subsequent addition of $HC\equiv CC_6H_4CO_2Me$ (0.005 g, 0.029 mmol) in DCM (2 cm³) and continual stirring for 16 h at ambient temperature resulted in the formation of a yellow suspension. The mixture was filtered and solvent removed under reduced pressure. ³¹P{¹H} and ¹H NMR spectroscopy demonstrated formation of **22a**. The resultant product was redissolved in DCM (5 cm³), with subsequent addition of a solution of KO^tBu (0.122 g, 1.09 mmol) in MeOH (10 cm³) resulting in the formation of a yellow precipitate. ³¹P{¹H} and ¹H NMR spectroscopy demonstrated formation of **22b** and **22c**.

5.3.4 ATTEMPTED INSTALLATION OF PHOSPHAALKENE TERMINI

Attempted synthesis of $[RuCl(dppe)_2(C\equiv CC(OSiMe_3)=P(SiMe_3))]$

Method A: To a suspension of **22b** (0.106 g, 0.104 mmol) in THF (10 cm³) cooled to -80 °C was added a standard solution of LiP(TMS)₂ (2.22 cm³, 0.047 M in THF) with continual stirring. The mixture was allowed to warm to ambient temperature over 3 h. ³¹P{¹H} and ¹H NMR spectroscopy of the crude product showed the presence of starting materials only.

Method B: To a suspension of **22b** (0.086 g, 0.085 mmol) in Et₂O (10 cm³) was added a standard solution of LiP(TMS)₂ (2.32 cm³, 0.036 M in Et₂O) drop-wise at ambient temperature with continual stirring. The mixture was stirred for 48 h. ³¹P{¹H} and ¹H NMR spectroscopy of the crude product showed the presence of starting materials only.

Method C: To a suspension of **22b** (0.143 g, 0.141 mmol) in DME (5 cm³) was added P(TMS)₃ (0.04 cm³, 0.141 mmol) at –30 °C with continual stirring. The mixture was allowed to warm to ambient temperature over 48 h. No reaction was observed by ³¹P{¹H} and ¹H NMR spectroscopy of an aliquot of the crude product. ³¹P{¹H} and ¹H NMR spectroscopy of the crude product showed the presence of starting materials only.

Method D: To a solution of LiP(TMS)₂ (7.33 cm³, 0.047 M in THF) in THF (5 cm³) at –72 °C was added a solution of **22a** (0.400g, 0.343 mmol) in THF (5 cm³) with continual stirring, with a colour change from pale yellow to orange/red observed. The mixture was allowed to warm to ambient temperature over 1 h, with gradual formation of a yellow precipitate. Formation of **22b** was confirmed by ³¹P{¹H} and ¹H NMR spectroscopy.

Method E: To a solution of **22a** (0.300 g, 0.257 mmol) in THF (10 cm³) was added a standard solution of P(TMS)₃ (6.99 cm³, 0.037 M in THF) at ambient temperature with continual stirring. The mixture was stirred for 16 h with formation of a peach-coloured precipitate. ¹H (CDCl₃) δ_H: 3.72 (s, OCH₃), 3.58 (m (br), CH). ³¹P{¹H} (CDCl₃) δ_P: 48.8 (d $J_{PP} = 27.34$ Hz), dppe), –98.2 (qnt ($J_{PP} = 27.34$ Hz), P(SiMe₃)₃).

5.3.5 ATTEMPTED SYNTHESIS OF TUNGSTEN AND MOLYBDENUM PROPARGYLIDYNE COMPLEXES TERMINATING IN CO₂Me AND SiMe₃

Attempted synthesis of [W(≡CC≡CCO₂Me){OC(O)CF₃}(CO)₂(tmeda)]

Method A: To a solution of HC≡CCO₂Me (0.12 cm³, 1.33 mmol) in THF (30 cm³) at –30 °C was added ⁿBuLi (0.53 cm³, 2.5 M in hexanes), drop-wise, and the mixture stirred for 20 min. Subsequently, W(CO)₆ (0.470 g, 1.33 mmol) was added to the solution and the mixture allowed to warm to ambient temperature over 1 h, with a gradual colour change to dark brown. The solution was cooled to –78 °C before drop-wise addition of (CF₃CO)₂O (0.18 cm³, 1.33 mmol). The mixture was allowed to warm to –50 °C before drop-wise addition of tmeda (0.20 cm³, 1.33 mmol). Evolution of CO was observed. The mixture was allowed to warm to ambient temperature over 2 h. Solvent was removed under reduced pressure. ¹H NMR spectroscopy revealed an intractable mixture of products.

Method B: To a solution of HC≡CCO₂Me (0.13 cm³, 1.48 mmol) in THF (30 cm³) at –80 °C was added ⁿBuLi (0.59 cm³, 2.5 M in hexanes), drop-wise, and the mixture stirred for 15 min. Subsequently, W(CO)₆ (0.522 g, 1.48 mmol) was added to the solution and the mixture allowed

to warm to ambient temperature over 1 h, with a gradual colour change to red/brown. The solution was cooled to $-78\text{ }^{\circ}\text{C}$ before drop-wise addition of $(\text{CF}_3\text{CO})_2\text{O}$ (0.21 cm^3 , 1.48 mmol). The mixture was allowed to warm to $-50\text{ }^{\circ}\text{C}$ before drop-wise addition of tmeda (0.22 cm^3 , 1.48 mmol). Evolution of CO was observed. The mixture was allowed to warm to ambient temperature over 1 h. Solvent was removed under reduced pressure. ^1H NMR spectroscopy revealed an intractable mixture of products.

Attempted synthesis of $[\text{Mo}(\equiv\text{CC}\equiv\text{CCO}_2\text{Me})\{\text{OC}(\text{O})\text{CF}_3\}(\text{CO})_2(\text{tmeda})]$

Method A: To a solution of $\text{HC}\equiv\text{CCO}_2\text{Me}$ (0.21 cm^3 , 2.38 mmol) in THF (30 cm^3) at $-30\text{ }^{\circ}\text{C}$ was added $^n\text{BuLi}$ (0.95 cm^3 , 2.5 M in hexanes), drop-wise, and the mixture stirred for 25 min. Subsequently, $\text{Mo}(\text{CO})_6$ (0.628 g, 2.38 mmol) was added to the solution and the mixture allowed to warm to ambient temperature over 1 h, with a gradual colour change to dark brown. The solution was cooled to $-78\text{ }^{\circ}\text{C}$ before drop-wise addition of $(\text{CF}_3\text{CO})_2\text{O}$ (0.33 cm^3 , 2.38 mmol). The mixture was allowed to warm to $-50\text{ }^{\circ}\text{C}$ before drop-wise addition of tmeda (0.36 cm^3 , 2.38 mmol). Evolution of CO was observed. The mixture was allowed to warm to ambient temperature over 1 h. Solvent was removed under reduced pressure. ^1H NMR spectroscopy revealed an intractable mixture of products.

Method B: To a solution of $\text{HC}\equiv\text{CCO}_2\text{Me}$ (0.12 cm^3 , 1.36 mmol) in THF (30 cm^3) at $-80\text{ }^{\circ}\text{C}$ was added $^n\text{BuLi}$ (0.54 cm^3 , 2.5 M in hexanes), drop-wise, and the mixture stirred for 30 min. Subsequently, $\text{Mo}(\text{CO})_6$ (0.360 g, 1.36 mmol) was added to the solution and the mixture allowed to warm to ambient temperature over 1 h, with a gradual colour change to red/brown. The solution was cooled to $-78\text{ }^{\circ}\text{C}$ before drop-wise addition of $(\text{CF}_3\text{CO})_2\text{O}$ (0.20 cm^3 , 1.36 mmol). The mixture was allowed to warm to $-50\text{ }^{\circ}\text{C}$ before drop-wise addition of tmeda (0.20 cm^3 , 1.36 mmol). Evolution of CO was observed. The mixture was allowed to warm to ambient temperature over 1 h. Solvent was removed under reduced pressure. ^1H NMR spectroscopy revealed an intractable mixture of products.

Attempted synthesis of $[\text{Tp}^\text{Mo}(\text{CO})_2(\equiv\text{CC}\equiv\text{CCO}_2\text{Me})]$*

To a solution of $\text{HC}\equiv\text{CCO}_2\text{Me}$ (0.08 cm^3 , 0.881 mmol) in THF (30 cm^3) at $-30\text{ }^{\circ}\text{C}$ was added $^n\text{BuLi}$ (0.35 cm^3 , 2.5 M in hexanes), drop-wise, and the mixture stirred for 25 min. Subsequently, $\text{W}(\text{CO})_6$ (0.310 g, 0.881 mmol) was added to the solution and the mixture allowed to warm to ambient temperature over 1 h, with a gradual colour change to dark brown. The solution was cooled to $-78\text{ }^{\circ}\text{C}$ before drop-wise addition of $(\text{CF}_3\text{CO})_2\text{O}$ (0.12 cm^3 , 0.881 mmol). Evolution of CO was observed. The mixture was stirred for 30 min before addition of KTp^* (0.300 g, 0.881 mmol) and subsequently allowed to warm to ambient temperature over 1 h. Solvent was removed under reduced pressure. ^1H NMR spectroscopy revealed an intractable

mixture of products. The solid product was redissolved in THF and passed through an alumina column with THF as the eluent. Solvent was removed under reduced pressure, yielding a yellow solid product. ^1H NMR spectroscopy revealed an intractable mixture of products.

Attempted synthesis of $[\text{Tp}^\text{Mo}(\text{CO})_2(\equiv\text{CC}\equiv\text{CCO}_2\text{Me})]$*

To a solution of $\text{HC}\equiv\text{CCO}_2\text{Et}$ (0.15 cm^3 , 1.48 mmol) in THF (30 cm^3) at $-75\text{ }^\circ\text{C}$ was added $^n\text{BuLi}$ (0.59 cm^3 , 2.5 M in hexanes), drop-wise, and the mixture stirred for 1 h. Subsequently, $\text{Mo}(\text{CO})_6$ (0.392 g, 1.48 mmol) was added to the solution and the mixture allowed to warm to ambient temperature over 1 h, with a gradual colour change to red. The solution was cooled to $-75\text{ }^\circ\text{C}$ before drop-wise addition of $(\text{CF}_3\text{CO})_2\text{O}$ (0.21 cm^3 , 1.48 mmol). The mixture was stirred for 30 min. before addition of KTp^* (0.506 g, 1.48 mmol) and subsequently allowed to warm to ambient temperature over 1 h. Solvent was removed under reduced pressure. ^1H NMR spectroscopy revealed an intractable mixture of products. The solid product was redissolved in THF and passed through an alumina column with THF as the eluent. Solvent was removed under reduced pressure, yielding a yellow solid product. ^1H NMR spectroscopy revealed an intractable mixture of products.

*Synthesis of $[\text{TpW}(\text{CO})_2(\equiv\text{CC}\equiv\text{CSiMe}_3)]$ (**29**)*

Compound **29** was prepared by a modified literature procedure. In a typical preparation, $^n\text{BuLi}$ (1.1 cm^3 , 2.5 M in hexanes) was added drop-wise to a solution of $\text{HC}\equiv\text{CSiMe}_3$ (0.40 cm^3 , 2.84 mmol) in THF (30 cm^3) at $-30\text{ }^\circ\text{C}$ and the mixture stirred for 30 min. Subsequently, $\text{W}(\text{CO})_6$ (1.00 g, 2.84 mmol) was added to the solution and the mixture allowed to warm to ambient temperature over 1 h. The solution was cooled to $-75\text{ }^\circ\text{C}$ before drop-wise addition of $(\text{CF}_3\text{CO})_2\text{O}$ (0.40 cm^3 , 2.84 mmol). The mixture was stirred for 30 min before addition of KTp (0.73 g, 2.84 mmol) and subsequently allowed to warm to ambient temperature over 1 h. The mixture was passed through an alumina column with THF as the eluent. ^1H NMR (CD_2Cl_2) δ_{H} : 8.02 (2 H, d ($^3J_{\text{HH}} = 1.56\text{ Hz}$), Pz-CH), 7.73 (2 H, d ($^3J_{\text{HH}} = 1.95\text{ Hz}$), Pz-CH), 7.66 (1 H, d ($^3J_{\text{HH}} = 1.95\text{ Hz}$), Pz-CH), 7.64 (1 H, d ($^3J_{\text{HH}} = 1.56\text{ Hz}$), Pz-CH), 6.32 (2 H, t ($^3J_{\text{HH}} = 2.34\text{ Hz}$), Pz- H^4), 6.20 (1 H, t ($^3J_{\text{HH}} = 2.34\text{ Hz}$), Pz- H^4), 0.22 (9 H, s, $\text{Si}(\text{CH}_3)_3$).

*Synthesis of $[\text{TpMo}(\text{CO})_2(\equiv\text{CC}\equiv\text{CSiMe}_3)]$ (**30**)*

Compound **30** was prepared by a modified literature procedure. In a typical preparation, $^n\text{BuLi}$ (1.1 cm^3 , 2.5 M in hexanes) was added drop-wise to a solution of $\text{HC}\equiv\text{CSiMe}_3$ (0.40 cm^3 , 2.84 mmol) in THF (30 cm^3) at $-30\text{ }^\circ\text{C}$ and the mixture stirred for 30 min. Subsequently, $\text{W}(\text{CO})_6$ (1.00 g, 2.84 mmol) was added to the solution and the mixture allowed to warm to ambient

temperature over 1 h. The solution was cooled to $-75\text{ }^{\circ}\text{C}$ before drop-wise addition of $(\text{CF}_3\text{CO})_2\text{O}$ (0.40 cm^3 , 2.84 mmol). The mixture was stirred for 30 min. before addition of KTp (0.97 g , 2.84 mmol) and subsequently allowed to warm to ambient temperature over 1 h. The mixture was passed through an alumina column with THF as the eluent. ^1H NMR (CD_2Cl_2) δ_{H} : 7.91 (2 H, d ($^3J_{\text{HH}} = 1.95\text{ Hz}$), Pz-CH), 7.73 (2 H, dd ($J_{\text{HH}} = 2.34, 0.78\text{ Hz}$), Pz-CH), 7.65 (1 H, d ($^3J_{\text{HH}} = 2.34\text{ Hz}$), Pz-CH), 7.55 (1 H, d ($^3J_{\text{HH}} = 1.95\text{ Hz}$), Pz-CH), 6.29 (2 H, t ($^3J_{\text{HH}} = 2.34\text{ Hz}$), Pz- H^4), 6.17 (1 H, t ($^3J_{\text{HH}} = 2.34\text{ Hz}$), Pz- H^4), 0.23 (9 H, s, $\text{Si}(\text{CH}_3)_3$).

Synthesis of $[\text{Tp}^\text{W}(\text{CO})_2(\equiv\text{CC}\equiv\text{CSiMe}_3)]$ (**31**)*

Compound **31** was prepared by a modified literature procedure. In a typical preparation, $^n\text{BuLi}$ (1.5 cm^3 , 2.5 M in hexanes) was added drop-wise to a solution of $\text{HC}\equiv\text{CSiMe}_3$ (0.53 cm^3 , 3.78 mmol) in THF (30 cm^3) at $-30\text{ }^{\circ}\text{C}$ and the mixture stirred for 30 min. Subsequently, $\text{Mo}(\text{CO})_6$ (1.00 g , 3.78 mmol) was added to the solution and the mixture allowed to warm to ambient temperature over 1 h. The solution was cooled to $-75\text{ }^{\circ}\text{C}$ before drop-wise addition of $(\text{CF}_3\text{CO})_2\text{O}$ (0.53 cm^3 , 3.78 mmol). The mixture was stirred for 30 min. before addition of KTp (0.98 g , 3.78 mmol) and subsequently allowed to warm to ambient temperature over 1 h. The mixture was passed through an alumina column with THF as the eluent. ^1H NMR (CD_2Cl_2) δ_{H} : 5.89 (2 H, s (br), Pz- H^4), 5.82 (1 H, s (br), Pz- H^4), 2.57 (6 H, s, Pz-CH), 2.36 (6 H, s, Pz-CH), 2.31 (3 H, s, Pz-CH), 2.30 (3 H, s, Pz-CH), 0.17 (9 H, s, $\text{Si}(\text{CH}_3)_3$).

Synthesis of $[\text{Tp}^\text{Mo}(\text{CO})_2(\equiv\text{CC}\equiv\text{CSiMe}_3)]$ (**32**)*

Compound **32** was prepared by a modified literature procedure. In a typical preparation, $^n\text{BuLi}$ (1.5 cm^3 , 2.5 M in hexanes) was added drop-wise to a solution of $\text{HC}\equiv\text{CSiMe}_3$ (0.53 cm^3 , 3.78 mmol) in THF (30 cm^3) at $-30\text{ }^{\circ}\text{C}$ and the mixture stirred for 30 min. Subsequently, $\text{Mo}(\text{CO})_6$ (1.00 g , 3.78 mmol) was added to the solution and the mixture allowed to warm to ambient temperature over 1 h. The solution was cooled to $-75\text{ }^{\circ}\text{C}$ before drop-wise addition of $(\text{CF}_3\text{CO})_2\text{O}$ (0.53 cm^3 , 3.78 mmol). The mixture was stirred for 30 min. before addition of KTp* (1.30 g , 3.78 mmol) and subsequently allowed to warm to ambient temperature over 1 h. The mixture was passed through an alumina column with THF as the eluent. ^1H NMR (CD_2Cl_2) δ_{H} : 5.84 (2 H, s (br), Pz- H^4), 5.83 (1 H, s (br), Pz- H^4), 2.53 (6 H, s, Pz-CH), 2.35 (6 H, s, Pz-CH), 2.31 (3 H, s, Pz-CH), 2.30 (3 H, s, Pz-CH), 0.18 (9 H, s, $\text{Si}(\text{CH}_3)_3$).

5.3.6 CROSS-COUPLING REACTIONS

Attempted synthesis of complexes of the type $[Tp'M(CO)_2(≡CC≡CCO_2Me)]$ via Sonogashira coupling reactions

I: To a stirring suspension of **30** (0.040 g, 0.084 mmol), $IC_6H_4CO_2Me$ (0.022 g, 0.084 mmol), $[PdCl_2(PPh_3)_2]$ (0.006 g, 0.008 mmol) and CuI (0.002 g, 0.008 mmol) in DMF (5 cm³) was added NEt_3 (0.12 cm³, 0.8 mmol) and the mixture heated to 60 °C for 5 min with subsequent addition of TBAF (0.026 cm³, 0.084 mmol). The mixture was heated to 60 °C for a further 2 h before filtering through a glass fibre filter paper and solvent removed under reduced pressure. No reaction was observed, determined by NMR spectroscopy.

II: To a stirring suspension of **32** (0.360 g, 0.645 mmol), $IC_6H_4CO_2Me$ (0.170 g, 0.645 mmol), $[PdCl_2(PPh_3)_2]$ (0.045 g, 0.064 mmol) and CuI (0.012 g, 0.064 mmol) in DMF (5 cm³) was added NEt_3 (0.90 cm³, 6.45 mmol) and the mixture heated to 60 °C for 5 min with subsequent addition of TBAF (0.20 cm³, 0.690 mmol). The mixture was heated to 60 °C for a further 2 h before filtering through a glass fibre filter paper and solvent removed under reduced pressure. No reaction was observed, determined by NMR spectroscopy.

III: To a stirring suspension of **31** (0.250 g, 0.387 mmol), $IC_6H_4CO_2Me$ (0.100 g, 0.387 mmol), $[PdCl_2(PPh_3)_2]$ (0.027 g, 0.039 mmol) and CuI (0.002 g, 0.039 mmol) in DMF (5 cm³) was added NEt_3 (0.54 cm³, 3.87 mmol) and the mixture heated to 60 °C for 5 min with subsequent addition of TBAF (0.12 cm³, 0.400 mmol). The mixture was heated to 60 °C for a further 2 h before removal of solvent under reduced pressure. No reaction was observed, determined by NMR spectroscopy.

IV: To a stirring suspension of **32** (0.205 g, 0.367 mmol), $IC_6H_4CO_2Me$ (0.096 g, 0.367 mmol), $[PdCl_2(PPh_3)_2]$ (0.026 g, 0.037 mmol) and CuI (0.007 g, 0.037 mmol) in DMF (5 cm³) was added NEt_3 (0.51 cm³, 3.67 mmol) and the mixture heated to 60 °C for 5 min with subsequent addition of TBAF (0.12 cm³, 0.400 mmol). The mixture was heated to 60 °C for a further 16 h before removal of solvent under reduced pressure. An intractable mixture of products was formed with ¹H NMR spectroscopic resonances unable to be assigned.

V: A stirring suspension of **32** (0.175 g, 0.314 mmol), $IC_6H_4CO_2Me$ (0.082 g, 0.314 mmol), $[PdCl_2(PPh_3)_2]$ (0.044 g, 0.063 mmol) and CuI (0.012 g, 0.063 mmol) in NEt_3 (0.20 cm³) was heated to reflux for 5 min with subsequent addition of TBAF (0.35 mL, 0.314 mmol). The mixture was heated to reflux for a further 1 h, then allowed to cool to ambient temperature for 24 h. Solvent was removed under reduced pressure. An intractable mixture of products was formed, with ¹H NMR spectroscopic resonances unable to be assigned.

VI: K_2CO_3 (0.097 g, 0.700 mmol) and **30** (0.311 g, 0.656 mmol) were suspended in

MeOH:THF (1:1) (10 cm³) and the mixture stirred at ambient temperature for 45 min. The mixture was filtered into a stirring suspension of IC₆H₄CO₂Me (0.172 g, 0.656 mmol), [Pd(PPh₃)₄] (0.151 g, 0.131 mmol) and CuI (0.012 g, 0.066 mmol) in THF (10 cm³) and the mixture heated to reflux for 3 h. The mixture was allowed to cool to ambient temperature for 16 h. An intractable mixture of products was observed in a ¹H NMR spectrum of the crude product. The remaining mixture was filtered and the resultant solution washed in DCM:H₂O (1:1), dried over MgSO₄, filtered through Celite® and solvent removed under reduced pressure. No change was observed in the ¹H NMR spectrum of the resultant solid product to that of the crude product.

VII: A stirring suspension of **32** (0.285 g, 0.511 mmol), IC₆H₄CO₂Me (0.134 g, 0.511 mmol), K₂CO₃ (0.730 g, 0.529 mmol), [Pd(PPh₃)₄] (0.072 g, 0.051 mmol) and CuI (0.010 g, 0.051 mmol) in MeOH:THF (1:1) (10 cm³) was heated to reflux for 3 h. The mixture was then allowed to cool to ambient temperature for 16 h. An intractable mixture of products was observed in a ¹H NMR spectrum of the crude product. The remaining mixture was filtered and the resultant solution washed in DCM:H₂O (1:1), dried over MgSO₄, filtered through Celite® and solvent removed under reduced pressure. No change was observed in the ¹H NMR spectrum of the resultant solid product to that of the crude product.

VIII: A stirring suspension of **30** (0.245 g, 0.517 mmol), IC₆H₄CO₂Me (0.135 g, 0.517 mmol), KOH (0.290 g, 5.17 mmol), [PdCl₂(PPh₃)₂] (0.072 g, 0.103 mmol) and CuI (0.098 g, 0.052 mmol) in IPA (20 cm³) was heated to reflux for 5 h. An intractable mixture of products was observed in a ¹H NMR spectrum of the crude product.

IX: A stirring suspension of **32** (0.228 g, 0.403 mmol), IC₆H₄CO₂Me (0.106 g, 0.403 mmol), KOH (0.226 g, 4.03 mmol), [PdCl₂(PPh₃)₂] (0.056 g, 0.081 mmol) and CuI (0.009 g, 0.040 mmol) in IPA (20 cm³) was heated to reflux for 5 h. An intractable mixture of products was observed in a ¹H NMR spectrum of the crude product. The remaining mixture was filtered and concentrated to *ca.* 10 cm³ with subsequent addition of DCM (5 cm³). The mixture was passed through an alumina column and eluted with DCM:hexane (5:1) and solvent removed under reduced pressure. No change was observed in the ¹H NMR spectrum of the resultant solid product to that of the crude product.

X: A stirring suspension of **30** (0.366 g, 0.772 mmol), IC₆H₄CO₂Me (0.202 g, 0.772 mmol), KOH (0.432 g, 7.72 mmol), [Pd(PPh₃)₄] (0.178 g, 0.154 mmol) and CuI (0.015 g, 0.077 mmol) in IPA (20 cm³) was heated to reflux for 5 h. An intractable mixture of products was observed in a ¹H NMR spectrum of the crude product. The remaining mixture was filtered and the resultant solution washed in DCM:H₂O (2:3), dried over MgSO₄, filtered through fluted filter paper and solvent removed under reduced pressure. An intractable mixture of products was observed in a ¹H NMR spectrum of the resultant solid.

XI: A stirring suspension of **30** (0.262 g, 0.553 mmol), IC₆H₄CO₂Me (0.150 g, 0.553 mmol),

KOH (0.310 g, 5.53 mmol), [Pd(PPh₃)₄] (0.128 g, 0.111 mmol) and CuI (0.010 g, 0.055 mmol) in IPA (20 cm³) was heated to reflux for 16 h. An intractable mixture of products was observed in a ¹H NMR spectrum of the crude product. The remaining mixture was filtered and concentrated to *ca.* 10 cm³ with subsequent addition of DCM (5 cm³). The mixture was passed through an alumina column and eluted with DCM:hexane (5:1) and solvent removed under reduced pressure. No change was observed in the ¹H NMR spectrum of the resultant solid product to that of the crude product.

XII: A stirring suspension of **32** (0.310 g, 0.556 mmol), IC₆H₄CO₂Me (0.150 g, 0.556 mmol), KOH (0.310 g, 5.56 mmol), [PdCl₂(PPh₃)₂] (0.078 g, 0.011 mmol) and CuI (0.011 g, 0.056 mmol) in IPA (20 cm³) was heated to reflux for 3 h. The mixture was allowed to cool to ambient temperature for 24 h. An intractable mixture of products was observed in a ¹H NMR spectrum of the crude product. The remaining mixture was diluted with DCM (5 cm³), filtered and washed hexane. Solvent was removed under reduced pressure.

XIII: A stirring suspension of **32** (0.309 g, 0.554 mmol), IC₆H₄CO₂Me (0.145 g, 0.554 mmol), KOH (0.310 g, 5.54 mmol), [Pd(PPh₃)₄] (0.128 g, 0.011 mmol) and CuI (0.011 g, 0.055 mmol) in IPA (15 cm³) was heated to reflux for 5 h. The mixture was allowed to cool to ambient temperature for 16 h. An intractable mixture of products was observed in a ¹H NMR spectrum of the crude product.

XIV: A stirring suspension of **32** (0.388 g, 0.695 mmol), IC₆H₄CO₂Me (0.182 g, 0.695 mmol), KOH (0.389 g, 6.95 mmol), [Pd(PPh₃)₄] (0.161 g, 0.014 mmol) and CuI (0.013 g, 0.070 mmol) in IPA (20 cm³) was heated to reflux for 3 h. The mixture was allowed to cool to ambient temperature for 72 h. An intractable mixture of products was observed in a ¹H NMR spectrum of the crude product.

XV: A stirring suspension of **30** (0.284 g, 0.600 mmol), IC₆H₄CO₂Me (0.157 g, 0.600 mmol), KOH (0.336 g, 6.00 mmol), [Pd(PPh₃)₄] (0.139 g, 0.120 mmol) and CuI (0.011 g, 0.060 mmol) in IPA (20 cm³) was heated to reflux for 3 h. The mixture was allowed to cool to ambient temperature for 48 h. An intractable mixture of products was observed in a ¹H NMR spectrum of the crude product. The remaining mixture was filtered and the resultant solution washed in DCM:H₂O (2:3), dried over Na₂SO₄, filtered through fluted filter paper and solvent removed under reduced pressure. An intractable mixture of products was observed in a ¹H NMR spectrum of the resultant solid.

XVI: A stirring suspension of **30** (0.301 g, 0.635 mmol), IC₆H₄CO₂Me (0.138 g, 0.635 mmol), KOH (0.360 g, 6.35 mmol), [Pd(PPh₃)₄] (0.150 g, 0.127 mmol) and CuI (0.012 g, 0.064 mmol) in IPA (30 cm³) was heated to reflux for 3 h. The mixture was allowed to cool to ambient temperature for 168 h. An intractable mixture of products was observed in a ¹H NMR spectrum of the crude product. The remaining mixture was filtered and the resultant solution washed in DCM:H₂O (2:3), dried over MgSO₄, filtered through Celite® and solvent removed under

reduced pressure. An intractable mixture of products was observed in a ^1H NMR spectrum of the resultant solid.

XVII: A stirring suspension of **32** (0.306 g, 0.548 mmol), $\text{IC}_6\text{H}_4\text{CO}_2\text{Me}$ (0.119 g, 0.548 mmol), KOH (0.307 g, 5.48 mmol), $[\text{Pd}(\text{PPh}_3)_4]$ (0.130 g, 0.110 mmol) and CuI (0.010 g, 0.055 mmol) in IPA (20 cm^3) was heated to reflux for 3 h. The mixture was allowed to cool to ambient temperature for 72 h. An intractable mixture of products was observed in a ^1H NMR spectrum of the crude product. The remaining mixture was filtered before addition of analytical grade MeOH (4 cm^3), NaI (0.16 g, 1.10 mmol) and Merrifield's resin (0.300 g, 8.22 mmol). The mixture was stirred at ambient temperature for 24 h and subsequently filtered, with solvent removed under reduced pressure. No change was observed in the ^1H NMR spectrum of the resultant solid product to that of the crude product.

XVIII: A stirring suspension of **29** (0.292 g, 0.520 mmol), $\text{IC}_6\text{H}_4\text{CO}_2\text{Me}$ (0.136 g, 0.520 mmol), KOH (0.291 g, 5.20 mmol), $[\text{Pd}(\text{PPh}_3)_4]$ (0.120 g, 0.104 mmol) and CuI (0.010 g, 0.052 mmol) in IPA (15 cm^3) was heated to reflux for 3 h. The mixture was allowed to cool to ambient temperature for 48 h. An intractable mixture of products was observed in a ^1H NMR spectrum of the crude product. The remaining mixture was filtered and the resultant solution washed in DCM: H_2O (2:3), dried over MgSO_4 , filtered through Celite® and solvent removed under reduced pressure. An intractable mixture of products was observed in a ^1H NMR spectrum of the resultant solid.

Attempted synthesis of $[\text{TpW}(\text{CO})_2(\text{C}\equiv\text{CCCO}_2\text{Me})]$ via $[\text{TpW}(\text{CO})_2(\text{C}\equiv\text{CCAuPPh}_3)]$

$[\text{TpW}(\text{CO})_2(\text{C}\equiv\text{CCAuPPh}_3)]$ (**33**) (0.32 g, 0.337 mmol), $\text{IC}_6\text{H}_4\text{CO}_2\text{Me}$ (0.088 g, 0.337 mmol), $[\text{Pd}(\text{PPh}_3)_4]$ (0.08 g, 0.067 mmol) and CuI (0.007 g, 0.034) were dissolved in THF (15 cm^3) and the mixture heated to reflux for 4 h. The mixture was subsequently allowed to cool for *ca.* 1 h before being filtered and solvent removed under reduced pressure, furnishing a red/brown solid.

5.4 EXPERIMENTAL DETAILS FOR CHAPTER 4

5.4.1 SYNTHESIS OF COMPLEXES η^1 -PHOSPHAALKYNE COMPLEXES **34–39**

*Synthesis of [Ru(dppe)₂(C \equiv CCO₂Me)(P \equiv C(SiMe₃))][OTf] (**34**)*

[RuCl(dppe)₂(C \equiv CCO₂Me)] (**22b**) (0.300 g, 0.295 mmol) and AgOTf (0.076 g, 0.295 mmol) were dissolved in DCM (5 cm³) at ambient temperature with continual stirring, yielding a light purple suspension. The mixture was stirred for 10 min before addition of TMSC \equiv P (6.80 cm³, 0.043 M in toluene). The suspension was stirred for 1 h, then filtered yielding an orange/red solution. Solvent was removed under reduced pressure. The sticky brown solid was dissolved in DCM (10 cm³) and solvent removed under reduced pressure yielding a copper coloured, powdered solid. Yield: 0.224 g, 0.180 mmol, 61%. $\nu_{\text{max}}/\text{cm}^{-1}$ 1265 (CP), 1680 (CO), 2098 (CC). Anal. Found: C, 58.59%; H, 4.75%. Calcd for C₆₁H₆₀P₅O₅F₃SiSRu: C, 58.79%; H, 4.82%. ¹H-NMR (CDCl₃): δ_{H} 7.40 (12 H, m, C₆H₅), 7.33 (4 H, m, C₆H₅), 7.19 (8 H, m, C₆H₅), 7.10 (16 H, m, C₆H₅), 3.65 (3 H, s, CH₃), 2.82 (8 H, m, C₂H₄), -0.12 (9 H, s, Si(CH₃)₃). ¹³C{¹H}-NMR (CDCl₃): δ_{C} 192.6 (d (¹J_{CP} = 89.93 Hz), C \equiv P), 152.7 (s, C=O), 133.7 (m (br), C₆H₅), 132.9 (m (br), C₆H₅), 132.2 (dqnt (*J* = 209.41, 11.55 Hz), C₆H₅), 131.0 (d (*J* = 29.39 Hz), C₆H₅), 128.5 (m (br), C₆H₅), 128.3 (m (br), C₆H₅), 120.8 (m (br) Ru–C \equiv C), 108.8 (d (br) (³J_{CP} = 24.4 Hz), Ru–C \equiv C), 51.7 (s, CH₃), 29.9 (qnt (²J_{CP} = 11.8 Hz), C₂H₄), 0.3 (s, Si(CH₃)₃). ³¹P{¹H}-NMR (CDCl₃): δ_{P} 108.4 (qnt (²J_{PP} = 35.0 Hz), P \equiv C), 41.2 (d (²J_{PP} = 35.0 Hz), PPh₂). ²⁹Si{¹H}-NMR (CDCl₃) δ_{Si} : -12.3. Crystal data for **52**: colourless prisms, 0.14 x 0.12 x 0.06 mm³, C₆₁H₆₀F₃O₅P₅RuSSi, *a* = 27.1458(6) Å, *b* = 12.4837(3) Å, *c* = 18.8950(5) Å, α = 90°, β = 102.193(2)°, γ = 90°, *U* = 6258.7(3) Å³, monoclinic, *Cc*, *Z* = 4, total reflections = 46877, independent reflections = 13387, *R*_{int} = 0.0829, θ_{max} = 27.07, *R*₁ [*I* > 2σ(*I*)] = 0.077, *wR*₂ = 0.2030 and 741 parameters, CCDC 962351.²⁹¹

*Synthesis of [Ru(dppe)₂(CCCO₂Et)(P \equiv C(SiMe₃))][OTf] (**35**)*

Prepared in a similar fashion to that described for **34** from **23b** (0.365 g, 0.354 mmol), AgOTf (0.091 g, 0.354 mmol) and TMSCP (8.15 cm³, 0.043 M in toluene). Yield: 0.257 g, 0.204 mmol, 58%. Anal. Found: C, 58.85%; H, 4.92%. Calcd for C₆₂H₆₂P₅O₅F₃SiSRu: C, 59.09%; H, 4.92%. $\nu_{\text{max}}/\text{cm}^{-1}$ 1265 (CP), 1672 (CO), 2087 (CC). ¹H-NMR (CDCl₃): δ_{H} 7.44 (12 H, m, C₆H₅), 7.35 (4 H, m, C₆H₅), 7.21 (8 H, m, C₆H₅), 7.13 (16 H, m, C₆H₅), 4.13 (2 H, q (³J_{HH} = 7.16 Hz), OCH₂), 2.85 (8 H, m, C₂H₄), 1.30 (3 H, t (³J_{HH} = 7.16 Hz), CH₃), -0.09 (9 H, s, Si(CH₃)₃). ¹³C{¹H}-NMR (CDCl₃): δ_{C} 192.4 (d, (¹J_{CP} = 88.67), C \equiv P), 152.4 (s, C=O), 133.3 (dqnt (*J* = 81.6, 2.0 Hz), C₆H₅), 132.5 (dqnt (*J* = 206.0, 10.8 Hz), *ipso*-C₆H₅), 131.1 (d (*J* = 32.3 Hz),

C_6H_5), 128.4 (dqnt ($J = 22.5, 2.3$ Hz), C_6H_5), 119.8 (dqnt ($^2J_{PP} = 92.9, 17.7$ Hz), $Ru-C\equiv C$), 109.0 (d (br) ($^3J_{CP} = 21.7$ Hz), $Ru-C\equiv C$), 60.5 (s, OCH_2), 29.9 (qnt ($^2J_{CP} = 11.7$ Hz), C_2H_4), 14.6 (s, CH_3), -0.1 (s, $Si(CH_3)_3$). $^{31}P\{^1H\}$ -NMR ($CDCl_3$): δ_P 108.6 (qnt ($^2J_{PP} = 33.6$ Hz), $P\equiv C$), 41.2 (d ($^2J_{PP} = 33.6$ Hz), PPh_2). $^{29}Si\{^1H\}$ -NMR ($CDCl_3$) δ_{Si} : -9.9.

*Synthesis of $[Ru(dppe)_2(C\equiv CPh)(P\equiv C(SiMe_3))][OTf]$ (**36**)*

Prepared in a similar fashion to that described for **34** from **24b** (0.168 g, 0.163 mmol), AgOTf (0.042 g, 0.163 mmol) and TMSCP (5.34 cm³, 0.031 M in toluene). Anal Found: C, 61.55; H, 5.03. Calcd for $C_{62}H_{62}P_5O_5F_3SiSRu$: C, 61.76; H, 4.91. ν_{max}/cm^{-1} 1265 (CP), 2024 (CC). 1H NMR ($CDCl_3$) δ_H : 7.67 (8 H, m (br), C_6H_5), 7.36 (8 H, dt ($J = 24.75, 7.54$ Hz), C_6H_5), 7.26 (1 H, s (br), Ph), 7.24 (2 H, d (br) ($J = 7.54$ Hz), Ph), 7.17 (8 H, t ($J = 7.68$ Hz), C_6H_5), 7.07 (16 H, m, C_6H_5), 6.82 (2 H, d (br) ($J = 7.46$ Hz), Ph), 2.86 (8 H, m, C_2H_4), -0.11 (9 H, s, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ_C : 188.6 (d ($^1J_{CP} = 88.0$), $C\equiv P$), 133.5 (dqnt ($J = 173.8, 11.3$ Hz), *ipso*- C_6H_5), 133.4 (dqnt ($J = 123.3, 2.4$ Hz), C_6H_5), 130.9 (d (br) ($J = 1.9$ Hz), C_6H_5), 129.3 (m (br), C_6H_4), 128.3 (dqnt ($J = 16.9, 2.2$ Hz), C_6H_5), 126.2 (s (br), C_6H_4), 116.2 (d (br) ($J_{CP} = 23.6$ Hz), $Ru-C\equiv C$), 108.5 (dqnt ($^3J_{CP} = 94.7, ^2J_{CP} = 17.7$ Hz), $Ru-C\equiv C$), 30.6 (quint. ($^2J_{CP} = 11.4$ Hz), C_2H_4), 0.4 (s, $Si(CH_3)_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ_P : 112.5 (quint. ($J_{PP} = 33.1$), $P\equiv C$), 42.4 (d ($J_{PP} = 33.1$), PPh_2). $^{29}Si\{^1H\}$ NMR ($CDCl_3$) δ_{Si} : -13.2.

*Synthesis of $[Ru(dppe)_2(C\equiv CC_6H_4CO_2Me)(P\equiv C(SiMe_3))][OTf]$ (**37**)*

Prepared in a similar fashion to that described for **34** from **25b** (0.302 g, 0.277 mmol), AgOTf (0.071 g, 0.277 mmol) and TMSCP (6.12 cm³, 0.045 M in toluene). Yield: 0.147 g, 0.144 mmol, 52%. Anal. Found: C, 60.75%; H, 4.85%. Calcd for $C_{67}H_{64}P_5O_5F_3SiSRu$: C, 60.86%; H, 4.84%. ν_{max}/cm^{-1} 1248 (CP), 2066 (CC). 1H NMR ($CDCl_3$) δ_H : 7.89 (2 H, d ($^3J_{HH} = 8.14$ Hz), C_6H_4), 7.57 (8 H, m (br), C_6H_5), 7.38 (8 H, dt ($J = 31.61, 7.43$ Hz), C_6H_5), 7.18 (8 H, m, C_6H_5), 7.04 (16 H, m, C_6H_5), 6.76 (2 H, d ($J_{HH} = 8.14$ Hz), C_6H_4), 3.92 (3 H, s, OCH_3), 2.87 (8 H, m, C_2H_4), -0.10 (9 H, s, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ_C : 190.2 (m (br), $C\equiv P$), 167.0 (s, $C=O$), 134.0 (m, C_6H_5), 132.9 (m, C_6H_5), 131.5 (s, C_6H_4), 131.0 (d ($J = 8.7$ Hz), C_6H_5), 129.9 (s, C_6H_4), 129.6 (s, C_6H_4), 128.6 (m, C_6H_5), 128.4 (m, C_6H_5), 127.1 (s, C_6H_4), 116.0 (m (br), $Ru-C\equiv C$), 108.8 (m (br), $Ru-C\equiv C$), 52.2 (s, OCH_3), 30.5 (qnt ($^1J_{CP} = 11.5$ Hz), C_2H_4), 2.0 (s, $Si(CH_3)_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ_P : 111.0 (qnt ($^2J_{PP} = 33.0$ Hz), PPh_2), 41.8 (d ($^2J_{PP} = 33.0$ Hz), $P\equiv C$). $^{29}Si\{^1H\}$ -NMR ($CDCl_3$) δ_{Si} : -12.3.

Synthesis of [Ru(dppe)₂(C≡CC₆H₄CO₂Et)(P≡C(SiMe₃))][OTf] (38)

Prepared in a similar fashion to that described for **34** from **26b** (0.702 g, 0.635 mmol), AgOTf (0.163 g, 0.635 mmol) and TMSCP (9.51 cm³, 0.067 M in toluene). Yield: 0.558 g, 0.418 mmol, 66%. Anal Found: C, 61.20%; H, 4.95%. Calcd for C₆₈H₆₆P₅O₄F₃SiSRu: C, 61.12%; H, 4.94%. $\nu_{\max}/\text{cm}^{-1}$ 1269 (CP), 1706 (CO), 2087 (CC). ¹H NMR (CDCl₃) δ_{H} : 7.91 (2 H, d (³J_{HH} = 8.01 Hz) C₆H₄), 7.57 (8 H, s (br), C₆H₅), 7.26 (8 H, dt (*J* = 30.62, 7.00 Hz), C₆H₅), 7.18 (8 H, m, C₆H₅), 7.05 (16 H, m, C₆H₅), 6.75 (2 H, d (³J_{HH} = 7.91 Hz), C₆H₄), 4.38 (2 H, q (³J_{HH} = 7.14 Hz), CH₂), 2.87 (8 H, m (br), C₂H₄), 1.41 (3 H, t (³J_{HH} = 7.14 Hz), CH₃), -0.10 (9 H, s, Si(CH₃)₃). ¹³C{¹H} NMR (CDCl₃) δ_{C} : 190.3 (m (br), C≡P), 166.5 (s, C=O), 133.2 (m, *ipso*-C₆H₅), 134.0 (m, C₆H₅), 132.9 (m, C₆H₅), 131.4 (s, C₆H₄), 131.0 (d (*J* = 7.8 Hz), C₆H₅), 129.9 (s, C₆H₄), 129.6 (s, C₆H₄), 128.6 (m, C₆H₅), 128.4 (m, C₆H₅), 125.4 (s, C₆H₄), 116.0 (m (br), Ru-C≡C), 61.1 (s, OCH₂), 30.5 (qnt (¹J_{CP} = 11.6 Hz), C₂H₄), 14.52 (s, CH₃), -0.47 (m (br), Si(CH₃)₃). ³¹P{¹H} NMR (CDCl₃) δ_{P} : 111.1 (qnt (²J_{PP} = 33.2 Hz), P≡C), 41.6 (d (²J_{PP} = 33.2 Hz), PPh₂). ²⁹Si{¹H} NMR (CDCl₃) δ_{Si} : -11.0

Synthesis of [Ru(dppe)₂(C≡CC₆H₄OMe)(P≡C(SiMe₃))][OTf] (39)

Prepared in a similar fashion to that described for **34** from **27b** (0.210 g, 0.198 mmol), AgOTf (0.051 g, 0.198 mmol) and TMSCP (3.75 cm³, 0.053 M in toluene). Anal. Found: C, 61.00%; H, 4.94%. Calcd for C₆₅H₆₄P₅O₄F₃SiSRu: C, 60.89%; H, 5.00%. $\nu_{\max}/\text{cm}^{-1}$ 1265 (CP), 2040 (CC). ¹H NMR (CDCl₃) δ_{H} : 7.67 (8 H, s (br), C₆H₅), 7.40–7.31 (8 H, dt (*J* = 21.80, 7.42 Hz), C₆H₅), 7.18–7.05 (24 H, dt (*J* = 38.90, 7.42 Hz), C₆H₅), 6.77 (4 H, m (br), C₆H₄), 3.83 (3 H, s, OCH₃), 2.84 (8 H, m (br), C₂H₄), -0.12 (9 H, s, Si(CH₃)₃). ¹³C{¹H} NMR (CDCl₃) δ_{C} : 188.2 (d (*J*_{CP} = 86.8 Hz), C≡P), 158.2 (s (br), *para*-C₆H₄), 133.6 (dqnt (²J_{CP} = 176.9, 11.1 Hz), *ipso*-C₆H₅), 133.5 (dqnt (*J* = 127.1, 2.3 Hz), C₆H₅), 131.3 (qnt (br) (*J* = 1.4 Hz), C₆H₄), 130.9 (s (br), C₆H₅), 128.4 (dqnt (*J* = 17.3, 2.3 Hz), C₆H₅), 119.6 (m (br), *ipso*-C₆H₄), 115.9 (d (br) (³J_{CP} = 23.0 Hz), Ru-C≡C), 114.0 (s (br), C₆H₄), 104.7 (d (br) (²J_{CP} = 83.6 Hz), Ru-C≡C), 55.4 (s, OCH₃), 30.8 (qnt (¹J_{CP} = 11.6 Hz), C₂H₄), 0.51 (d (³J_{CP} = 11.6 Hz), Si(CH₃)₃). ³¹P{¹H} NMR (CDCl₃) δ_{P} : 113.1 (qnt (²J_{PP} = 31.9 Hz), P≡C), 42.2 (d (²J_{PP} = 31.9 Hz), PPh₂). ²⁹Si{¹H} NMR (CDCl₃) δ_{Si} : -13.3.

5.4.2 SYNTHESIS OF TERMINAL CYAPHIDE COMPLEXES **40–45***Synthesis of [Ru(dppe)₂(C≡CCO₂Me)(C≡P)] (40)*

[Ru(dppe)₂(C≡CCO₂Me)(P≡C(SiMe₃))][OTf] (**34**) (0.190 g, 0.153 mmol) and KO^tBu (0.017 g, 0.153 mmol) were dissolved in THF (5 cm³) at ambient temperature with continual stirring. The solution was stirred for 1 h with a small amount of precipitate formed. The solution was filtered and solvent removed under reduced pressure, yielding a beige solid. Yield: 0.094 g, 0.092 mmol, 60 %. $\nu_{\max}/\text{cm}^{-1}$ 1253 (CP), 1660 (CO), 2036 (CC). Anal. Found: C, 61.98%; H, 4.74%. Calcd for C₅₆H₅₁P₅O₂Ru: C, 58.13%; H, 4.41%. ¹H NMR (CD₂Cl₂): δ_{H} 7.63 (6 H, m (br), C₆H₅), 7.38 (6 H, m (br), C₆H₅), 7.29 (6 H, t ($J_{\text{HH}} = 7.5$ Hz), C₆H₅), 7.22 (6 H, t ($J_{\text{HH}} = 7.5$ Hz), C₆H₅), 7.10 (8 H, t ($J_{\text{HH}} = 7.5$ Hz), C₆H₅), 7.01 (8 H, t ($J_{\text{HH}} = 7.5$ Hz), C₆H₅), 3.53 (3 H, s, CH₃), 2.86 (4 H, m (br), C₂H₄), 2.67 (4 H, m (br), C₂H₄). ¹³C{¹H} NMR (CD₂Cl₂): δ_{C} 279.1 (m (br), C≡P), 153.0 (s, C=O), 143.8 (m (br), Ru–C≡C), 136.5 (m (br), C₆H₅), 134.7 (m (br), C₆H₅), 135.1 (d ($J = 37.0$ Hz), C₆H₅), 127.7 (m (br), C₆H₅), 127.5 (m (br), C₆H₅), 112.4 (s, Ru–C≡C), 51.2 (s, OCH₃), 31.3 (qnt ($^1J_{\text{CP}} = 12.0$ Hz), C₂H₄). ³¹P{¹H} NMR (CD₂Cl₂): δ_{P} 168.5 (s (br), P≡C), 49.7 (d ($J_{\text{PP}} = 3.8$ Hz), PPh₂). MS [ESI⁺]: m/z (%): 983 (100), 1009 [$\text{M}^+ - \text{CH}_3$], 983 [$\text{M}^+ - \text{CP}$].

Synthesis of [Ru(dppe)₂(C≡CCO₂Et)(C≡P)] (41)

Prepared in a similar fashion to that described for **40** from **35** (0.191 g, 0.152 mmol) and KO^tBu (0.017 g, 0.152 mmol). Yield: 0.097 g, 0.093 mmol, 61%. $\nu_{\max}/\text{cm}^{-1}$ 1253 (CP), 1656 (CO), 2044 (CC). ¹H NMR (CD₂Cl₂): δ_{H} 7.65 (8 H, m, C₆H₅), 7.39 (8 H, m, C₆H₅), 7.31 (4 H, t ($J = 7.20$ Hz), C₆H₅), 7.23 (4 H, t ($J = 7.2$ Hz), C₆H₅), 7.12 (8 H, t ($J = 7.7$ Hz), C₆H₅), 7.03 (8 H, t ($J = 7.8$ Hz), C₆H₅), 4.01 (2 H, q ($^3J_{\text{HH}} = 7.2$ Hz), OCH₂), 2.87 (4 H, m (br), C₂H₄), 2.69 (4 H, m (br), C₂H₄), 1.26 (3 H, t ($^3J_{\text{HH}} = 7.2$ Hz), CH₃). ¹³C{¹H} NMR (CD₂Cl₂): δ_{C} 278.7 (m (br), C≡P), 152.0 (s, C=O), 141.8 (m (br), Ru–C≡C), 135.5 (dqnt ($J = 111.2, 10.3$ Hz), *ipso*-C₆H₅), 134.9 (m (br), C₆H₅), 134.1 (qnt ($J = 2.3$ Hz), C₆H₅), 129.0 (d ($J = 39.8$ Hz), C₆H₅), 127.0 (dqnt ($J = 27.2, 2.1$ Hz), C₆H₅), 112.0 (s, Ru–C≡C), 59.1 (s, OCH₂), 30.7 (qnt ($J_{\text{CP}} = 11.8$ Hz), C₂H₄), 14.5 (s, CH₃). ³¹P{¹H} NMR (CD₂Cl₂): δ_{P} 168.5 (m (br), P≡C), 49.8 (d ($^3J_{\text{PP}} = 4.9$ Hz), PPh₂). MS [ESI⁺]: m/z (%): 995 (100), 1036 [$\text{M}^+ - \text{H}$].

*** Elemental analysis data for compound **41** is inaccurate due to the persistence of an NMR silent impurity in the product.

Synthesis of [Ru(dppe)₂(C≡CPh)(C≡P)] (42)

Prepared in a similar fashion to that described for **40** from **36** (0.040 g, 0.031 mmol) and KO^tBu (0.004 g, 0.031 mmol). $\nu_{\max}/\text{cm}^{-1}$ 1239 (CP), 1901 (CC). ¹H NMR (CD₂Cl₂) δ_{H} : 7.61 (8 H, m (br), C₆H₅), 7.54 (8 H, m (br), C₆H₅), 7.44 (2 H, dd (J = 30.0, 6.6 Hz), Ph), 7.24 (8 H, dt (J = 31.1, 7.4 Hz), C₆H₅), 7.13 (1 H, s (br), *para*-Ph), 7.03 (16 H, dt (J = 43.4, 7.7 Hz), C₆H₅), 6.76 (2 H, d (J = 7.3 Hz), Ph), 2.79 (8 H, dm (J = 94.8 Hz), C₂H₄). ¹³C{¹H} (CD₂Cl₂) δ_{C} : 281.5 (m (br), C≡P), 136.9 (dqnt (J = 168.9, 10.40 Hz), *ipso*-C₆H₅), 136.4 (m (br), C₆H₅), 135.0 (m (br), C₆H₅), 130.6 (s, C₆H₄), 130.4 (s, *ortho*-C₆H₄), 129.5 (d (J = 17.2 Hz), *meta*-C₆H₅), 128.1 (s, *para*-C₆H₄), 127.6 (m (br), C₆H₅), 127.4 (m (br), C₆H₅), 123.9 (s, *ipso*-C₆H₄), 119.8 (m (br), Ru–C≡C), 31.7 (quint. (¹ J_{CP} = 11.9 Hz), C₂H₄). ³¹P{¹H} NMR (CD₂Cl₂) δ_{P} : 160.6 (s (br), P≡C), 50.9 (d (J_{PP} = 4.0 Hz), PPh₂). MS [ESI⁺]: m/z (%): 905 (100), 1026 [M^+ + H – CH₃]. A resonance for C _{α} could not be assigned.

Synthesis of [Ru(dppe)₂(C≡CC₆H₄CO₂Me)(C≡P)] (43)

Prepared in a similar fashion to that described for **40** from **37** (0.191 g, 0.152 mmol) and KO^tBu (0.017 g, 0.152 mmol). $\nu_{\max}/\text{cm}^{-1}$ 1269 (CP), 1710 (CO), 2054 (CC). ¹H (CD₂Cl₂) δ_{H} : 7.76 (2 H, d (³ J_{HH} = 8.21 Hz), C₆H₄), 7.62 (8 H, m, C₆H₅), 7.47 (8 H, m, C₆H₅), 7.24 (8 H, dt (J = 38.7, 7.1 Hz), C₆H₅), 7.02 (16 H, dt (J = 58.2, 7.1 Hz), C₆H₅), 6.88 (2 H, d (³ J_{HH} = 8.21 Hz), C₆H₄), 3.87 (3 H, s, CH₃), 2.89 (4 H, m, C₂H₄), 2.67 (4 H, m, C₂H₄). ¹³C{¹H} (CD₂Cl₂) δ_{C} : 280.7 (m (br), C≡P), 167.7 (s, C=O), 140.1 (m (br), Ru–C≡C), 136.7 (dqnt (J = 138.4, 9.9 Hz), *ipso*-C₆H₅), 135.4 (m (br), C₆H₅), 134.8 (m (br), C₆H₅), 135.1 (s, C₆H₄), 130.2 (s, C₆H₄), 129.7 (s, C₆H₄), 129.4 (d (J = 6.0 Hz), C₆H₅), 127.1 (m (br), C₆H₅), 127.5 (m (br), C₆H₅), 125.0 (s, C₆H₄), 120.3 (m (br), Ru–C≡C), 52.2 (s, CH₃), 31.6 (qnt (¹ J_{CP} = 11.2 Hz), C₂H₄). ³¹P{¹H} (CD₂Cl₂) δ_{P} : 165.4 (m (br), C≡P), 50.7 (d (³ J_{PP} = 2.5 Hz), PPh₂). MS [ESI⁺]: m/z (%): 1085 (100), 1085 [M^+ – CH₃], 1057 [M^+ – CP].

Synthesis of [Ru(dppe)₂(C≡CC₆H₄CO₂Et)(C≡P)] (44)

Prepared in a similar fashion to that described for **40** from **38** (0.191 g, 0.152 mmol) and KO^tBu (0.017 g, 0.152 mmol). $\nu_{\max}/\text{cm}^{-1}$ 1246 (CP), 1703 (CO), 2054 (CC). ¹H (CD₂Cl₂) δ_{H} : 7.77 (2 H, d (³ J_{HH} = 8.30 Hz), C₆H₄), 7.62 (8 H, m, C₆H₅), 7.48 (8 H, m, C₆H₅), 7.25 (8 H, dt (J = 38.2, 7.38 Hz), C₆H₅), 7.03 (16 H, dt (J = 57.9, 7.4 Hz), C₆H₅), 6.68 (2 H, d (³ J_{HH} = 8.30 Hz), C₆H₄), 4.34 (2 H, q (³ J_{HH} = 7.45 Hz), OCH₂), 2.90 (4 H, m, C₂H₄), 2.68 (4 H, m, C₂H₄), 1.40 (3 H, t (³ J_{HH} = 7.45 Hz), CH₃). ¹³C{¹H} (CD₂Cl₂) δ_{C} : 280.8 (m (br), C≡P), 167.21 (s, C=O), 139.8 (m (br), Ru–C≡C), 136.7 (dqnt (J = 137.6, 10.43 Hz), *ipso*-C₆H₅), 135.4 (m (br), C₆H₅), 134.8 (m (br), C₆H₅), 135.0 (s, C₆H₄), 130.2 (s, C₆H₄), 129.74 (s, C₆H₄), 129.4 (d (J = 10.7 Hz), C₆H₅), 127.7 (m (br), C₆H₅), 127.5 (m (br), C₆H₅), 125.4 (s, C₆H₄), 120.3 (m (br), Ru–C≡C), 61.0 (s,

OCH₂), 31.6 (qnt (¹J_{CP} = 11.8 Hz), C₂H₄), 14.8 (s, CH₃). ³¹P{¹H} (CD₂Cl₂) δ_P: 165.3 (m (br), C≡P), 50.6 (d (³J_{PP} = 2.7 Hz), PPh₂). MS [ESI⁺]: *m/z* (%): 1187 (100), 1099 [M⁺ – CH₃].

Synthesis of [Ru(dppe)₂(C≡CC₆H₄OMe)(C≡P)] (45)

Prepared in a similar fashion to that described for **40** from **39** (0.085 g, 0.066 mmol) and KO^tBu (0.007 g, 0.066 mmol). *v*_{max}/cm⁻¹ 1261 (CP), 2032 (CC). ¹H NMR (CD₂Cl₂) δ_H: 7.57 (8 H, dm (*J* = 26.4 Hz), C₆H₅), 7.23 (8 H, dt (*J* = 30.1, 7.4 Hz), C₆H₅), 7.03 (16 H, dt (*J* = 43.6, 7.5 Hz), C₆H₅), 6.69 (4 H, s (br), C₆H₄), 3.77 (3 H, s, OCH₃), 2.77 (8 H, dm (*J* = 92.8 Hz), C₂H₄). ¹³C{¹H} NMR (CD₂Cl₂) δ_C: 282.0 (m (br), C≡P), 156.9 (s, *para*-C₆H₄), 137.0 (dqnt (*J* = 169.4, 10.3 Hz), 135.4 (m (br), C₆H₅), 135.0 (m (br), C₆H₅), 131.3 (s (br), C₆H₄), 129.5 (d (*J* = 19.4 Hz), C₆H₅), 127.6 (m (br), C₆H₅), 127.4 (m (br), C₆H₅), 118.9 (m, Ru–C≡C), 55.7 (s, CH₃), 31.7 (qnt (¹J_{CP} = 12.1 Hz), C₂H₄), 1.4 (s, Si(CH₃)₃). ³¹P{¹H} NMR (CD₂Cl₂) δ_P: 161.5 (s (br), P≡C), 52.7 (d (*J*_{PP} = 3.91 Hz), PPh₂). MS [ESI⁺]: *m/z* (%): 1029 (100), 1057 [M⁺ – CH₃], 1029 [M⁺ + H – CH₃]. A resonance for the β-carbon of the alkynyl ligand is not resolvable in the ¹³C{¹H} NMR spectrum.

5.4.3 REACTIVITY STUDIES WITH COMPOUNDS **40–45**

Addition of KO^tBu/MeOH to 34, synthesising compound G

To a stirring solution of **34** (0.151 g, 0.121 mmol) in DCM (5 cm³) was added KO^tBu (0.058 g, 0.485 mmol) in MeOH (10 cm³) and the mixture stirred at ambient temperature for 1 h. Gradual formation of a bronze-coloured precipitate was observed. The mixture was filtered and the precipitate dried under reduced pressure. ¹H NMR δ_H: 8.51 (dqnt, *J*_{HP} = 20.8, 6.8 Hz). ¹³C{¹H} NMR (CD₂Cl₂) δ_C: 175.1. ³¹P{¹H} NMR (CD₂Cl₂) δ_P: 298.3 (qnt, *J*_{PP} = 7.9 Hz), 52.1 (d, *J*_{PP} = 7.9 Hz).

Addition of [RuHCl(CO)(PPh₃)₃] to 40

[RuHCl(CO)(PPh₃)₃] (0.052 g, 0.055 mmol) and **40** (0.056 g, 0.055 mmol) were suspended in THF (5 cm³) at ambient temperature and the mixture allowed to stir for 1 h. A gradual increase in solubility was observed over time. Solvent was removed under reduced pressure. No reaction was observed by ³¹P{¹H} and ¹H NMR spectroscopy, with only the presence of starting materials observed.

*Addition of [Pd(PPh₃)₄] to **41***

[Pd(PPh₃)₄] (0.112 g, 0.106 mmol) and **41** (0.110 g, 0.106 mmol) were suspended in THF (5 cm³) at ambient temperature and the mixture allowed to stir for 1.5 h. Solvent was removed under reduced pressure. No reaction was observed by ³¹P{¹H} and ¹H NMR spectroscopy, with only the presence of starting materials observed.

*Addition of [Pt(PPh₃)₂(C₂H₄)] to **40***

[Pt(PPh₃)₂(C₂H₄)] (0.036 g, 0.049 mmol) and **40** (0.050 g, 0.049 mmol) were suspended in THF (5 cm³) at ambient temperature and the mixture allowed to stir for 1 h. Solvent was removed under reduced pressure. No reaction was observed by ³¹P{¹H} and ¹H NMR spectroscopy, with only the presence of starting materials observed.

*Addition of [PdCl(C₃H₅)]₂ to **40***

[Pt(PPh₃)₂(C₂H₄)] (0.021 g, 0.057 mmol) and **40** (0.058 g, 0.057 mmol) were suspended in THF (5 cm³) at ambient temperature and the mixture allowed to stir for 1 h. Solvent was removed under reduced pressure. An intractable mixture of products was observed by ³¹P{¹H} and ¹H NMR spectroscopy.

*Addition of [AuCl(tht)] to **40***

[AuCl(tht)] (0.010 g, 0.030 mmol) and **40** (0.030 g, 0.030 mmol) were suspended in toluene (5 cm³) at ambient temperature and the mixture allowed to stir for 20 h. Solvent was removed under reduced pressure. No reaction was observed by ³¹P{¹H} and ¹H NMR spectroscopy, with only the presence of starting materials observed.

*Addition of [AuCl(PPh₃)] to **41***

Method A: [AuCl(PPh₃)] (0.032 g, 0.065 mmol) and AgBF₄ (0.013 g, 0.065 mmol) were dissolved in THF (5 cm³) at ambient temperature and the solution stirred for 5 min. A solution of **41** (0.067 g, 0.065 mmol) in THF (5 cm³) was added and a gradual colour change to yellow/green then orange was observed over time. The mixture was stirred for 1 h and subsequently filtered. Solvent was removed under reduced pressure. An intractable mixture of products was observed by ³¹P{¹H} and ¹H NMR spectroscopy.

Method B: [AuCl(PPh₃)] (0.039 g, 0.078 mmol) and AgBF₄ (0.015 g, 0.078 mmol) were dissolved in THF (5 cm³) at ambient temperature and the solution stirred for 5 min. The solution was cooled to -78 °C before addition of **41** (0.080 g, 0.078 mmol) in THF (5 cm³) and a gradual colour change to orange/brown was observed over time, with formation of a white precipitate.

The mixture was allowed to warm to ambient temperature over 1 h. The mixture was filtered and solvent was removed under reduced pressure. An intractable mixture of products was observed by $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectroscopy.

*Addition of $\text{BF}_3\cdot\text{Et}_2\text{O}$ to **41***

Method A: $\text{BF}_3\cdot\text{Et}_2\text{O}$ (0.013 cm^3 , 0.106 mmol) was added drop-wise to a stirring solution of **41** (0.110 g, 0.106 mmol) in THF (5 cm^3) at ambient temperature and the solution stirred for 1 h. A gradual colour change to dark orange was observed. Solvent was removed under reduced pressure. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ_{P} : 212.6 (qnt, $J_{\text{PP}} = 10.2\text{ Hz}$), 239.6 (qnt, $J_{\text{PP}} = 10.0\text{ Hz}$), 52.1 (d, $J_{\text{PP}} = 10.0\text{ Hz}$), 45.5 (d, $J_{\text{PP}} = 10.2\text{ Hz}$). $^{11}\text{B}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ_{B} : 19.1, -1.1. ^{19}F NMR (CD_2Cl_2) δ_{F} : -76.6 (s), -76.5 (s).

Method B: $\text{BF}_3\cdot\text{Et}_2\text{O}$ (0.008 cm^3 , 0.068 mmol) was added drop-wise to a stirring solution of **41** (0.070 g, 0.068 mmol) in THF (5 cm^3) at $-78\text{ }^\circ\text{C}$. The solution was allowed to warm to ambient temperature over 2 h with continual stirring. Solvent was removed under reduced pressure. Identical spectra were observed to that found for Method A.

*Addition of $\text{BF}_3\cdot\text{Et}_2\text{O}$ to **45***

$\text{BF}_3\cdot\text{Et}_2\text{O}$ (0.009 cm^3 , 0.075 mmol) was added drop-wise to a stirring solution of **45** (0.080 g, 0.075 mmol) in THF (5 cm^3) at ambient temperature. The solution was stirred for 1 h with a colour change to dark red, then brown, observed over time. Solvent was removed under reduced pressure. An intractable mixture of products was observed by $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectroscopy.

*Addition of BCl_3 to **41***

BCl_3 (0.12 cm^3 , 0.118 mmol) was added drop-wise to a stirring solution of **41** (0.122 g, 0.118 mmol) in THF (5 cm^3) at ambient temperature and the solution stirred for 1 h. Solvent was removed under reduced pressure. An intractable mixture of products was observed by $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectroscopy.

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APPENDIX